An Investigation in to Alternative Material and Manufacturing Solutions for Lightweighting Interior and Exterior Automotive Brightware

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Abstract

Existing literature for a variety of material and manufacturing techniques was reviewed, in order to find alternative solutions for lightweighting automotive brightware. Light alloys such as magnesium, aluminium and titanium were all investigated as alternatives to the current cast zinc parts. Additive layer manufacture and metal injection moulding were both found to have potential for lightweighting parts but were not suited overall to manufacturing brightware. After the initial literature review, using cast aluminium was investigated in more detail and experimental testing was completed on a range of alloys. Alloys of Al-Si, Al-Mg and Al-Zn were tested on their visual appearance, mechanical performance and corrosion resistance against existing zinc brightware. Anodising was also attempted on some these aluminium alloys but found to be unsuitable for Al-Si alloys. The surface roughness, gloss and hardness of these alloys was competitive with existing brightware. Anodising of Al-Mg and Al-Zn alloys increased their corrosion resistance significantly but not to the level of the current zinc brightware. This was attributed to the poor optimisation of the anodising procedure. Despite this, these alloys showed potential for much greater performance after anodising. However, the literature review of these alloys suggested that the castability of the Al-Mg and Al-Zn alloys could be a major concern for use in brightware.

Contents

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Chapter 1

Introduction

The automotive sector is consistently being challenged to increase the fuel efficiency of the vehicles they manufacture. Pressure from regulators and governments is driving a shift towards reducing emissions. The Paris Climate Agreement of 2015, which was signed by 160 countries, sets out the long-term goal of restricting the average increase in global temperatures to 2°C [1]. To achieve this goal, countries across the globe have agreed to significant drops in their emissions. The European Union has set targets of reducing greenhouse gas emissions 20% by 2020 (compared to 1990 levels). Significantly, the long-term EU goal is to cut emissions by 80-95% (based on 1990 levels) by 2050 [2].

According to UK government statistics, the transport sector became the largest source of greenhouse gases in the UK in 2016, accounting for 26% of total greenhouse gas emissions [3]. Therefore, it is clear that to meet the aforementioned ambitious emission reduction targets, the transport sector will have to make significant reductions in emissions output. For automotive manufacturers one of the key ways this can be achieved is by maximising weight reduction in their vehicles. A 10% mass reduction can achieve an improvement in the fuel efficiency of cars of 3-8%, depending on the vehicle [4][5]. An increase in fuel efficiency results in a decrease in emissions produced, as less fuel is consumed to travel the same distance.

For Aston Martin Lagonda, brightware is the name given to metal or metal finished parts that add to the aesthetics of the car. Brightware parts do not serve any major structural purpose. Brightware can be both exterior and interior and may be finished to a variety of styles. Traditionally, this

could include a high gloss chrome finish, but painting of the part or a satin finish may also be desired by a designer. Examples of these parts could include flashes and streaks down the outside of a vehicle, bezels around the speedometer and door handles. Parts are finished to a high surface finish and a variety of sizes. The largest individual pieces are exterior parts, such as side strakes that can be around 30cm long. Interior parts are generally smaller with a higher level of intricacy in design. All parts are characterised by minimal wall thicknesses to reduce the material used. Some of the detail on parts may be machined but others are coated with no secondary manufacturing processes after casting. Aston Martin currently uses high pressure die cast zinc parts for the vast majority of their brightware parts. Cast zinc alloys provide a variety of benefits but they are quite heavy. With a variety of brightware components across a single car, an alternative lightweight approach for brightware could yield a considerable cumulative mass reduction across a whole vehicle. Therefore, the main objective of this investigation is to examine different solutions for manufacturing brightware parts that would result in a weight saving. This decrease in vehicle mass would help contribute to a reduction in emissions.

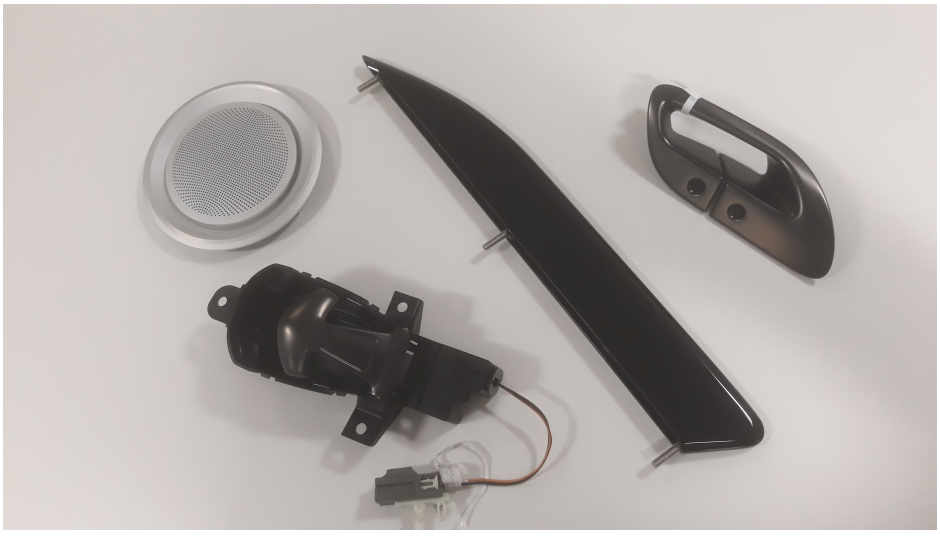

Figure 1.1: Typical examples of brightware parts

It is a vital requirement that any proposed alternative offers a weight saving over the existing solution. In addition to this, there are a few more critically important conditions that must also be completely satisfied. As brightware parts serve an aesthetic purpose ahead of a structural one, the

surface finish of the parts is vitally important. In addition, as multiple types of coatings or finishes may be applied to create a desired look for a part, the underlying part must be compatible with at least one usable coating. Ideally, the substrate would be compatible with a variety of coatings. Although brightware parts are not primarily structural components, the mechanical properties of the parts must not be completely overlooked. Hardness to resist scratches as well as necessary mechanical strength to resist deformation from aerodynamic or human forces are important considerations. Aston Martin cars likely to be kept running much longer than a standard car, due to the prestige, quality and collectability of the vehicle. The quality of the car must be maintained over this period. To keep the appearance over this extended time requires excellent corrosion protection and resistance to environmental attack. Cars could be shipped all over the world and encounter vastly different extremes of temperature and humidity. This must be considered when creating parts that are expected to remain consistent for the lifetime of the vehicle. There are a variety of other factors that could be considered including but not limited to: production rate, cost, ease of manufacture, toxicity and fracture/crash mechanisms. This investigation will attempt to take a holistic approach to analyse any alternatives across a variety of areas, instead of just focusing on one aspect of performance.

Chapter 2

Literature Review

The first step of this investigation was to complete a broad review in to the variety of techniques that could be used for lightweighting brightware components. The findings of this initial literature review are summarised in this chapter. The aim is to highlight a large variety of possible alternatives, looking at their advantages and disadvantages over the existing method, as well as their potential feasibility. The structure of this review means it can be considered in to two major sections. The materials section is focused on finding a direct material replacement for the current zinc alloy with a lighter material. The manufacturing section covers different production techniques that could lead to weight saving. There is some crossover between the sections. For example, any material studied in the materials section requires the capability to be processed by a route in the manufacturing section. Otherwise it would not be viable.

2.1 Materials

2.1.1 Requirements

Any material chosen for the application of brightware needs to satisfy various requirements. A few of the key requirements for a part are summarised below.

Any replacement material must have adequate mechanical properties. A lot of brightware parts are likely to be interacted with by a customer, so they

need to resist moderate forces that could expected from a human. Examples of this would include a part being leaned on by someone, or a handle component being pulled on. There are of course the forces exerted on a part while driving a car, especially at higher speeds. This factor is possibly more important to Aston Martin cars, as they have the capability to be driven at much higher speeds than the average car. These forces experienced while doing this will also likely be greater for exterior brightware. Gravel and loose stones being flicked up from the road present a chipping risk for exterior components.

The surface finish of the part is also very important. The surface roughness and reflectivity will normally be controlled to a greater extent by the manufacturing route, rather than the material. However, the compatibility of parts with a variety of coatings and finishes that may be applied, will often depend on the material. Whether any finish will provide a high-quality surface is also a material concern. At the moment, the finishes used by Aston Martin Lagonda on zinc brightware components are chrome plated (bright, satin and dark) and a few powder coated finishes. An anodised finish is also currently used on some wrought aluminium parts. The coating is important for protection and the aesthetics, so the substrate material needs to be compatible with a suitable surface finish.

Finally, corrosion resistance of the part is a major concern. Not only is there the potential for brightware to be exposed to a variety of different environments, that could accelerate the weathering process. The corrosion resistance of any part must be excellent, as even limited discolouration on the surface will be noticeable and unacceptable.

All the materials that are featured in the materials side of the review are lightweight metal alloys, excluding zinc. There is potential for polymer parts coated with a metal substrate or with a metal appearance/finish to be used for the application of brightware parts. Polymer parts would not provide the same mechanical properties as a metallic part. However, polymer parts don't corrode in the same manner as metallic one. Polymers are also much lighter than cast metal, so there would be a significant weight saving if utilised. These factors make polymer parts attractive for use as brightware and the use of polymer parts for similar applications is common across the automotive sector [6][7]. Aston Martin specified that using polymer parts was not in keeping with their design ethos and therefore, it was not a solution they wanted to pursue. Due to the main aim of the project being to investigate lightweight alternatives, it makes sense to review lightweight metals and their

alloys, as they could provide the largest reductions in mass. Zinc has also been included in the review to give some background to the reader on the current material choice.

2.1.2 Zinc

A zinc aluminium casting alloy is the current material choice for the majority of Aston Martin brightware already in use. The majority of cast zinc alloys are cast using high pressure die casting and this process has been utilised since 1914 [8]. The most common of zinc castings are based from a zinc aluminium alloy system where the eutectic point lies at around 5wt% Al content, depending on the specific alloy [9]. This aluminium content has a large effect on the mechanical properties and fluidity of the alloy.

The most widespread of the zinc aluminium casting alloys are a hypoeutectic alloy with an aluminium content of 4%. These alloys combine decent mechanical properties and a short freezing range of 5°C [9]. This short freezing range is beneficial for the fluidity of a casting. The conventional casting alloys, Zamak(US)/Mazak(UK) 2,3,5 and 7, are all based on the hypoeutectic aluminium alloy system. Zamak 7 is a higher purity version of Zamak 3 that gives it greater castability and a better surface finish, making it more used for decorative applications [9]. As well as having excellent fluidities, these die cast zinc alloys out perform some comparative aluminium castings across a variety of mechanical properties. The areas where these alloys are most competitive with aluminium are: impact strength, toughness and yield strength [9]. These alloys already have a short freezing range but by pushing the aluminium content up to a value closer to the eutectic point, the freezing range can be decreased even further. This in turn increases the castability even further, as the lower freezing range allows a melt to remain liquid and avoid the Mushy Zone for longer. This should also reduce the tendency for misruns to occur. Hypoeutectic zinc alloys with a higher aluminium content then 4% have been investigated for their enhanced fluidity. It was reported by J. Campbell, that according to F.E Goodwin, typical minimum section thicknesses for 4% Al alloys are 0.75mm, and this was improved to 0.3mm using a zinc aluminium alloy with 4.5wt% aluminium [8]. This increase in fluidity does come at the expense of lower impact strength, which peaks at 4.5wt% [9]. Zinc castings can be designed with wall thicknesses thinner than usually possible than for aluminium castings [9]. This intricacy of design also contributes to an excellent surface finish for zinc cast parts. The thin walls

and section thicknesses present in brightware components require an easily castable alloy such as zinc.

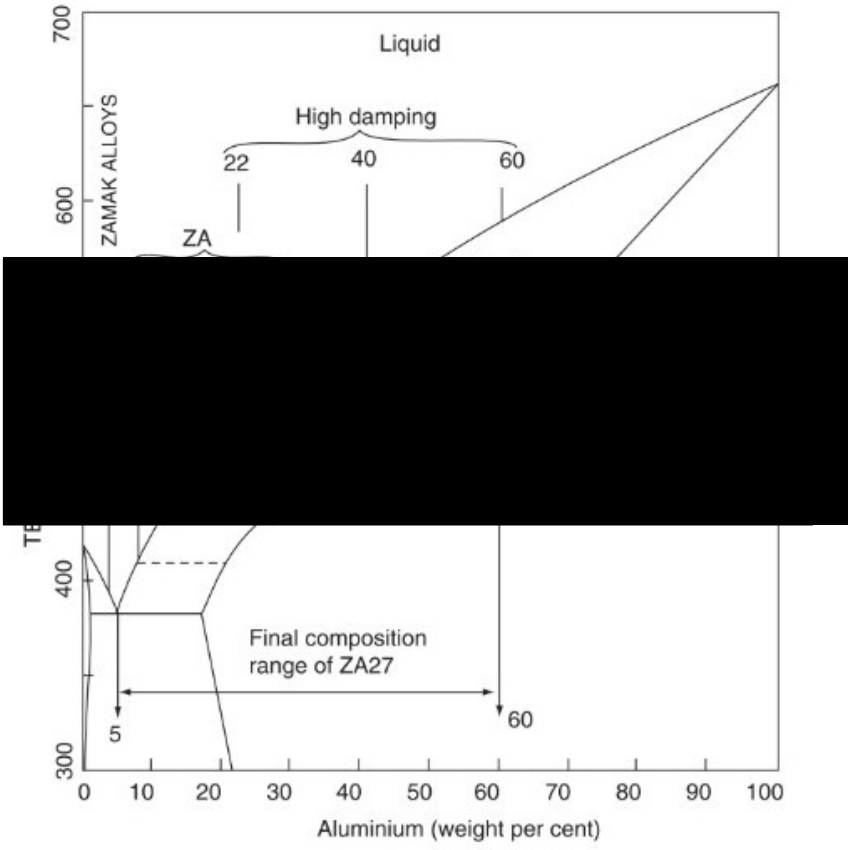

Figure 2.1: Zn-Al phase diagram [8]

Casting of hypereutectic zinc aluminium alloys is also possible, ZA27 is a zinc aluminium alloy containing 27wt% Al for enhanced wear resistance and high tensile strength [10]. The large increase in aluminium content comes with significant issues though. The much larger freezing range causes to an increase porosity within the casting. To remove the porosity encountered in a die cast ZA27, alternative manufacturing techniques such as squeeze casting or thixoforming can be used [11].

Various surface coatings and finishes can be applied to die cast zinc alloys, depending on the purpose of the coating. For decorative finishes, zinc die

castings may be painted, plated or have a chrome or phosphate conversion coating applied [12]. These coatings will also effect the surface wear resistance and corrosion resistance to varying amounts. For decorative chrome coatings that are currently used, chrome is plated over previously applied layers of copper and nickel. This final chrome layer is often very thin, only around 1 μm [13].

Zinc maintains excellent corrosion resistance due to the protection of from zinc oxide and hydroxide formed on the surface. These corrosion products occupy a larger volume than the substrate it replaces so cracks and scratches are healed over [14]. The corrosion resistance of zinc is increased further in atmospheric conditions when carbonate films form over the surface. Exposed sheet zinc has been found to have an effective outdoor life of 40 years [14]. When the flow of air to the surface is restricted, normally by water, the formation of the carbonate layer is not possible and the oxide and hydroxide products build up to create white rust. White rust is only loosely adherent and therefore, doesn't provide much corrosion protection [14]. Therefore, in damp and aqueous environments the corrosion rate of zinc and zinc alloys is vastly increased. The corrosion protection afforded by zinc means that half of the world consumption of zinc is for corrosion protection of steel [14].

The manufacturing cost for zinc castings can be lower than for similar aluminium castings. Cost of manufacture depends on a variety of factors and therefore, can be quite subjective. The lower melting point of zinc alloys, compared to aluminium alloys, reduces tool wear and increases die life [9]. It also means that less money is spent on the energy needed to melt zinc, rather than aluminium. Zinc is well suited to the application of decorative brightware due to its excellent castability, surface finish, corrosion resistance and low cost for die cast parts. The exceptional thin wall castability of zinc parts can be used by designers to reduce the weight of parts. The disadvantage of zinc alloys for casting are their weight and this review aims to identify possible alternative materials with much lower densities.

2.1.3 Aluminium

Aluminium alloys are already used in a variety of applications across cars. Wrought aluminium alloys of the 5000 and 6000 series have been used in body panels of cars in both exterior and interior locations [15]. 5000 series alloys contain magnesium as their main alloying addition, whereas the 6000

series also contain additions of silicon and magnesium. These alloys are generally corrosion resistant as the oxide film that forms on their surface during corrosion protects the metal underneath from further attack [16]. 5000 series alloys may be susceptible to Lüders bands which is especially undesirable on the visible panels of a car. Hence, the 6000 series with greater formability are preferred on exterior panels [17]. Aluminium alloys for body panels have the advantage of being lighter than steel alternatives. However, the 5000 and 6000 series of aluminium alloys are much more expensive than a zinc coated steel option, 3 times and 5 times more for 5000 and 6000 series alloys respectively [15].

Although wrought aluminium alloys are widespread in car design, from a manufacturing prospective, casting aluminium is more suitable for manufacturing brightware parts. This will be expanded on within the manufacturing section of this review. In short, casting parts allows for greater productivity and cost efficiency on greater volumes of parts. Cast aluminium alloys also already currently feature in modern automotive design. The most common cast alloys are the Aluminium-Silicon (Al-Si), Aluminium-Silicon-Magnesium (Al-Si-Mg) and Aluminium-Silicon-Copper (Al-Si-Cu) systems [18]. The choice of aluminium alloy for casting is dependent on the casting method as well as the final application of the part. Silicon increases the fluidity and therefore also the castability of the alloy. In addition, silicon reduces the overall shrinkage of the part during solidification and these castings generally have a good resistance to corrosion [18]. Typical uses for aluminium castings include engine blocks, wheels and suspension elements [17]. These elements contribute to a large proportion of the vehicle weight and therefore after ferrous metals, aluminium is generally the second most abundant metal used in a car [17].

Within the different types of used aluminium casting alloys, the Al-Si 300 and 400 series cast alloys have the highest castability [18]. This gives the greatest ability to cast intricate shapes and thin wall sections, which would useful for brightware parts. Within these groups there are specific alloys that favoured for high pressure die castings. These include A380 and A413 which are both Al-Si alloys [18]. For A380 the silicon content is 7.5wt%-9.5wt% whereas it is higher at 11wt%-13wt% for 413 [18]. The addition of silicon increases the hardness of the part which may be useful, but this also reduces the ease of which the part can be machined and polished. For a simple binary Al-Si alloy, the eutectic point occurs at 12.1% Si and 577°C [19]. For Al-Si-Cu alloys, there are no ternary compounds present [19]. The equilibrium phases can only be Al_2Cu and silicon. The ternary eutectic point for these alloys occurs at 520-525°C, which is around 50°C lower than for the binary

system. This will contribute to less mould wear and lower operating costs for the manufacture of the alloys, as the temperature requirements are not as high. However, the eutectic points for both these alloy systems is far greater than for the zinc aluminium alloys shown in the previous section. To operate at a higher temperature during manufacture will increase manufacturing cost as more energy will be required to keep the metal molten during casting.

Changes to the standard Al-Si alloys for high pressure die cast aluminium parts in cars have been developed, as manufacturers try to reduce the weight of the materials used in their vehicles. These include the Al-Si-Mg-Mn alloys [20]. Simple Al-Si alloys cannot be heat treated for improved mechanical properties as the silicon precipitates out from solid solution [18]. By increasing the strength of structural components, the size they are required to be can be reduced. The addition of magnesium allows for the heat treatment of the metal to improve the hardness by 2.5 times, compared to the original value. It also increases the tensile strength of the alloy [21]. This is due the presence of Mg_2Si precipitates among the aluminium dendrites, which act a barrier to dislocation movement and therefore any inhibit any deformation of the part. The number of precipitates can be increased by heat treatment of the alloys [21]. This ability to increase mechanical performance is excellent for reducing the weight of structural cast components. However, this is less relevant to the performance of aesthetic brightware parts.

Other notable cast aluminium alloys include the Aluminium-Copper and Aluminium-Magnesium systems. The Al-Cu alloys are specialised for performance in higher temperature applications. These alloys provide excellent toughness but lower corrosion resistance, due to the amount of copper [22]. Al-Mg alloys are generally very simple binary phase alloys with very few other additions. The strength of these alloys is their corrosion resistance. Al-Mg alloys see use in decorative applications as they can be machined, polished or anodised. However, they are less easily castable than the Al-Si alloys [22]. Another downside for aluminium casting is the high shrinkage possible during solidification which needs to be accounted for with careful mould design [18]. Aluminium castings also struggle with hydrogen pickup and bi-film formation [23] which are both factors to be controlled in casting.

Aluminium alloys generally not particularly sensitive to corrosion. This is important for brightware parts to increase the longevity of the car as much as possible. The electronegative potential for aluminium alloys is large compared to other metals, being more anodic than steel and zinc [24]. Although there is a large thermodynamic driving force for corrosion, aluminium gen-

erally shows strong resistance to corrosion. This is as during the initial electrochemical attack a strong oxide film is grown on the surface. This protects the metal underneath from further corrosion. The nature of the corrosion product and protective nature of the anodic film depends on the composition of the individual alloy corroding. Alloys are generally not sensitive to corrosion unless larger concentrations of copper are present in the microstructure [18]. This is due to the intermetallic particles that are precipitated near the grain boundaries in Al-Cu alloys [25]. Aluminium alloy A380 contains 3.5wt% copper [24] which may negatively affect the corrosion resistance of this alloy. This may make it unsuitable for brightware that requires excellent corrosion resistance. Otherwise, aluminium alloys show good resistance to general corrosion but are susceptible to pitting corrosion, if the oxide film is penetrated [24]. This is particularly dangerous in environments with high levels of chloride ions present, which is problematic for exterior brightware.

Corrosion performance of aluminium alloys can also be improved by the use of coatings and finishes. For decorative finishes of die cast aluminium paint and plate surfaces are possible [12]. For wrought aluminium, anodising is very popular and it is also possible with cast aluminium. However, the quality of anodising is dependent on the composition of the alloy and casting method. This is expanded on later in the investigation. Powder coating and chrome conversion coatings are also both possible with cast aluminium alloys [26]. These processes can be seen on alloy wheels. This is a useful reference point as the chrome high gloss finish of alloy wheels is comparable to some pieces of exterior brightware.

Aluminium alloys possess a variety of characteristics and properties that make them an attractive possibility for use in brightware components. Aluminium alloys are generally light with a with a typical density of 2.7 g/cm^3 [15]. Compared to the density of zinc casting alloys which have a density of 6.6-6.7gcm^3 [9], the density of aluminium alloys is very competitive. Aluminium also has a relatively low melting point for casting as well as parts formed by casting normally having a good surface finish [18], especially if manufactured using HPDC. This limits the amount of processing after casting which will lower cost. The corrosion resistance of aluminium alloys is also usual very good. These are all factors that make aluminium alloys an attractive alternative to zinc alloys for producing brightware parts.

2.1.4 Magnesium

Magnesium alloys include some of the lightest structural alloys with a density of 1.74g/cm^3 [27] and they have a higher strength to weight ratio than aluminium alloys [17]. This gives exceptional potential for lightweighting of brightware parts. In addition, magnesium alloys have excellent castability, with parts able to have wall thicknesses as low as 2mm [17]. Compared to aluminium alloys, magnesium alloys also have shorter cycle times when cast [28]. This means magnesium parts can be die cast up to 50% faster than equivalent aluminium parts, which creates an economic benefit. These factors make them an attractive option for low weight applications in the automotive sector. However, magnesium alloys are more expensive in raw material cost than aluminium [29]

Despite the positives for magnesium alloys, their use in the automotive sector has remained limited. Magnesium alloys have tended to only make up 0.5% of the weight of an average car in North America [29]. Historically, the largest single use of magnesium alloys for car manufacture was in the Volkswagen Beetle where they were utilised in the engine and transmission [27]. Apart from this magnesium alloys have only seen limited use within automotive manufacture including in: Instrument panel cross bars, dashboards, seats, steering wheels and transmission parts [4]. A more recent use of magnesium alloys in the automotive sector is in the centre console of the Porsche Carrera [30]. This is more promising as it is closer to a use of magnesium for a brightware part. Magnesium parts have possible uses across the car but are currently not fully utilised. An average car in North America contains only approximately 6kg of magnesium whereas there is the current technology to allow for almost 160kg [4]. Brightware could be one of the possible growth areas for the utilisation of magnesium.

A major drawback of magnesium alloys is their poor corrosion resistance. This is especially important for the application of brightware as the appearance of any part is vital. Magnesium alloys are so susceptible to corrosion due to the high electronegative potential of magnesium and the poor quality of any film produced by oxidation [28]. The electronegative potential of magnesium is more negative than aluminium, zinc and iron [24], which creates a large driving force for the corrosion of the alloy. Corrosion is sensitive to composition so occurs and is focused in the α phase first for Magnesium-Aluminium alloys. The α phase contains a lower percentage of aluminium which inhibits corrosion activity in magnesium. This selective attack a single phase leaves a honeycomb structure before the more aluminium rich phases

are attacked [31]. The other factor that contributes to such poor properties is the poor adherence of any protective film. The oxide/hydroxide layer that forms upon magnesium is soluble, even in humid conditions [28]. Therefore, it provides little to no protection to the metal below from subsequent corrosion in aqueous conditions.

If magnesium alloys are to see widespread use within the automotive sector, then their poor corrosion properties somehow needs to be overcome; this is not easy in practice. Many alloying additions are insoluble in magnesium, this includes additions to improve corrosion resistance [28]. Some metallurgy can be conducted to improve the corrosion resistance of magnesium alloys though. Additions of lithium and arsenic can cause passivisation of magnesium alloys [29] but these elements have major issues, especially with toxicity. There have been attempts to add other elements such as cerium to magnesium alloys to improve the strength of the surface film in hostile chloride environments [32]. Although this has had some success on specific alloys; in general, magnesium alloys perform very poorly in chloride environments.

The corrosion of magnesium alloys is affected by different scenarios and environments. Atmospheric or aqueous corrosion are the two major different systems for corrosion but within these categories there are number of variables. Some are relevant for both systems such as temperature. Whereas, factors such as the concentration of CO_2 gas in the atmosphere and the presence of any ions in solution are specific to either atmospheric or aqueous corrosion respectively. Both systems of corrosion could be important to the application of magnesium in brightware. For exterior brightware components, the amount of environmental attack would likely be much larger than for interior. The presence of rain, dirt, salt spray and acid rain is much more likely outside of the car.

For simple atmospheric corrosion, the performance of magnesium has been shown to be similar to that of mild steel, for a pure material or simple alloy [33]. MgO is the predominant corrosion product formed in dry ambient air on an exposed magnesium metal surface. MgO forms a thin compact film over the surface but the Pilling Bedworth ratio for MgO/Mg is smaller than one [33]. This means the volume of MgO formed over a surface is less than the volume of corroded material which leaves a porous oxide film. CO_2 content within an atmosphere increases the corrosion resistance of magnesium alloys as CO_2 is utilised to form a protective carbonate layer. The atmospheric corrosion rate of magnesium casting alloy AZ91D has been shown to decrease by 75% with 350ppm of CO_2 [34].

For an aqueous environment the surface film normally favoured is $Mg(OH)_2$ [33]. The films formed in aqueous conditions have some solubility in water, so they offer poor protection to the metal substrate [28]. In addition, as MgO is transformed in to $Mg(OH)_2$ in aqueous corrosion, the volume change between the oxide and hydroxide disrupts the surface film [33]. Finally, the dissolution rate of hydroxide film in aqueous corrosion is generally faster than the formation rate, so the surface film can't effectively heal itself [33]. These factors all contribute to the poor corrosion resistance of magnesium and magnesium alloys in aqueous environments. This would be a limiting factor for magnesium use in brightware. Especially, in exterior applications where the aqueous corrosion will be more prevalent.

As mentioned before, the role of aluminium in magnesium alloys is very important in corrosion resistance. Increasing the aluminium content of the alloy improves corrosion resistance but a lower limit of 2-4% Al is needed to create a significant drop in corrosion rate [34]. Other factors that affect corrosion rate include: a finer grain size [35], which reduces corrosion rate; and the level of impurities in the alloy, which has a positive correlation with the corrosion rate [24]. Salt is particularly damaging for magnesium alloys as the Na^+ and Cl^- ions are preserved on the surface. Both ions are not trapped within a corrosion product meaning they can remain and act like a catalyst for corrosion of the magnesium. Accelerating the rate of corrosion while also not being used up [34]. The large electronegativity of magnesium also means that is prone to galvanic corrosion when coupled or joined with another metal [29] . The susceptibility to aqueous and galvanic corrosion means that if magnesium brightware was to be used, special care would have to be taken in the design stage to minimise the risk of corrosion. This might include taking steps to avoid aqueous environments, more common with exterior brightware. It would also require care when attaching brightware parts to avoid promoting galvanic corrosion.

Any coating applied to cast magnesium alloys for use as brightware would require decorative surface finish and protective properties against corrosion and mechanical forces. A large variety of coatings can be applied to magnesium and some of these could be suitable. Electroplating of magnesium to deposit a chromium layer on the surface is possible with the correct pretreatment. Particular care must be taken with plating on magnesium alloys for a variety of reasons. One being as oxide films form rapidly on the surface in aqueous or atmospheric conditions. These layers prevent the proper bonding of the required undercoat layers [36]. Chromium based coatings are also becoming unfashionable due to their harmful nature in manufacture. There-

fore, alternative coatings to replace them are being investigated. Stannate based coatings are one such alternative and have the advantage that they can be self-healing. This ability to repair areas of mechanical or corrosive attack is dependent on the composition of the magnesium alloy substrate [37]. This functionality could be useful to limit the affect chips or scratches have on the corrosion resistance of a brightware part, which has the potential to extend the life cycle of a part.

Cast magnesium that could be of interest for use in brightware include the AZ91D and AZ91E alloys. These alloys are used for HPDC and gravity die casting respectively [38]. The alloys contain 9wt% aluminium, 1wt% zinc and have a low level of impurities. The higher purity of the AZ91D and E alloys over their predecessors gives them vastly improved corrosion resistance [15]. Another advantage of these alloys is their ability to be cast in very thin and intricate sections [15]. Both higher corrosion resistance and improved castability are appealing features for brightware.

2.1.5 Titanium

Titanium has a density of 4.43g/cm^3 [17], which is greater than for magnesium and aluminium. Therefore, while it is still classed as a lightweight alloy, it is considerably heavier for a part of a given size than aluminium and magnesium alternatives. Titanium would allow a weight saving on the existing cast zinc alloys that are used currently for the manufacture of brightware components. Other properties of titanium are strong corrosion resistance against multiple environments and attractive appearance [39]. The main quality of titanium is not necessarily the low weight of the metal but the relative mechanical performance for that low weight. The mechanical performance of brightware parts needs to reach an acceptable standard but the forces on these parts should not be particularly taxing.

Casting of titanium is possible, Ti-6Al-4V and Ti-5Al-2.5Sn are examples of alloys that are used [39]. The process of casting titanium must be carried out under a vacuum or controlled atmosphere at very high temperatures. This is very expensive and about 95% of titanium is wrought not cast [39]. This limits the ways brightware could be manufactured using titanium as a material.

One major downside to using titanium is the high material cost [39]. Further to that, titanium is difficult and expensive to machine. The low specific

heat capacity means heat isn't drawn away quickly from a cutting point and the mechanical properties of the titanium make it difficult to machine [40]. Waste of titanium from machining is also undesirable as the cost of titanium is much higher than the other lightweight metal alternatives. The cost and poor machinability of titanium have led to studies in to alternative manufacturing techniques, these include metal injection moulding. The quality of MIM titanium parts is limited by porosity and the pickup of atoms such as oxygen at interstitial sites. Porosity provides crack initiation sites and decreases the quality of surface finish, which is not desired for brightware parts. After sintering, a MIM part contains 3-4% porosity with optimised processing parameters [41]. This can be reduced to almost zero with the addition of a hot isostatic pressing stage after MIM [40]. Some porosity could be useful for reducing the weight of brightware parts, as long as the surface finish wasn't affected to severely.

It is difficult to find any reference to purely aesthetic titanium parts in automotive manufacture. This probably due to the unsuited nature of titanium to these applications. Brightware components should not require the advanced mechanical properties of titanium. Alternative materials could provide an acceptable level of performance at a lower weight with a much-reduced cost. There are some uses for titanium within the automotive sector. Titanium exhausts are viable due to their oxidation resistance which is not found in other lightweight alloys [17].

2.2 Manufacturing Process

2.2.1 Requirements

In order to select an appropriate processing method for the parts some assumptions about the requirements for the parts and the production volume need to be made. The table below displays the predicted production volumes for Aston Martin models

Table 2.1: Predicted production volumes for a variety of Aston Martin models

Model	2015	2016	2017	2018
GT Models	1800	2300	3500	3500
Sports Models	1800	1300	2300	2400
Total	3600	3600	5800	5900

Aston Martin were predicted to produce 5800 cars in 2017, over a variety of models. The predicted level of production increases in 2018 and this trend could well continue in to this year and beyond. The volume of production will have a massive effect on whether a manufacturing process is economically viable or not. Each Aston Martin has around 10-15 brightware components and these are normally unique to the vehicle. There isn't a large amount of sharing of parts between models as styling is unique for each model. Looking at this information, brightware parts will need to be produced in the range of tens of thousand but not in to the hundreds of thousand values. Other factors that will be controlled by the manufacturing process are the surface finish and dimensional tolerances. Both these variables must be kept to a high quality to keep to the high standards of Aston Martin Lagonda.

2.2.2 Die Casting

Die casting is an overarching term given to a variety of techniques where metal fills permanent moulds. The melt then solidifies in the mould which is opened, the part is ejected and the process is repeated. The pressure at which metal enters the mould defines the subprocess of die casting [23]. Gravity die casting only utilises the force of gravity to fill the casting, whereas low pressure and high pressure die casting use air or hydraulic pressure to force the metal in to the mould. Across the world, gravity die casting is often

referred to as die casting, gravity die casting or permanent mould casting. This is especially confusing as die casting and permanent mould casting can refer to different things across different sources. In this thesis the terms high pressure die casting and die casting will be used for the two different processes

The production volumes needed for brightware are around the value of tens of thousand, depending on the model being manufactured. There needs to be a very high reproducibility between all these parts. In addition, parts need to be manufactured to high tolerances and an excellent surface finish. Die casting gives high dimensional tolerances and good surface finish as a casting technique [42]. These tolerances and surface finish are obviously dependent on a variety of factors but a typical range for die casting as a process would be around 0.8–6.3 μm Ra [43]. Minimum wall thickness will also depend heavily on the castability of the alloy but values as low as 2mm are possible [43]. Some of the expected or typical tolerances for a given part size, are summarised in the figure 2.2.

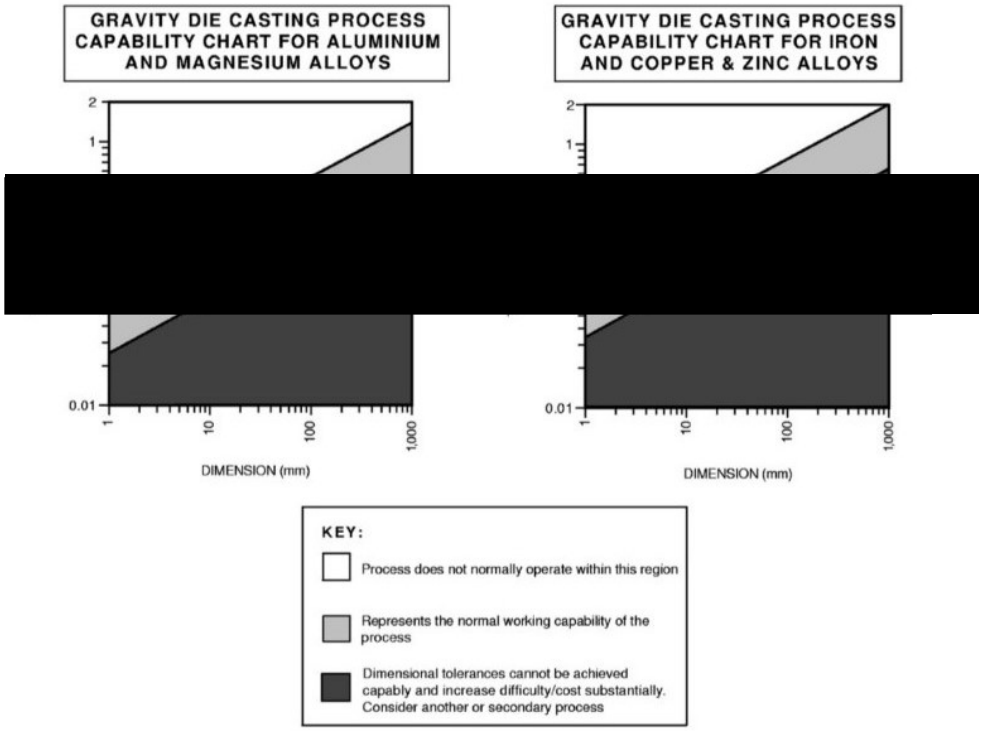

Figure 2.2: Representative tolerances for permanent mould casting [43]

The process of die casting is compatible with many different types of metal, including the light alloys of magnesium and aluminium that are mentioned in this review. Despite the great flexibility of the process, some metals are easier than other to cast. Generally low melting point alloys are cast in permanent moulds, such as zinc, aluminium and magnesium [44]. A higher melting temperature for an alloy may give a greater rate of mould wear. Some metals may need melting in a controlled atmosphere or with a vacuum to prevent the pickup of certain elements [39]. This has already been discussed for titanium in the materials section of this review.

Die casting can be used for the manufacture of parts of runs from 500 units to over 10,000 [23]. However, for low volume production the initial tooling makes the process far less competitive. There shouldn't be a problem with the economics of die casting for brightware parts because the anticipated production volumes are high enough to make the process viable. The sizes of parts can range from quite small at around 50g to 300kg in weight [43]. Brightware parts are likely to be closer to the lower range of weight for die cast products but remain perfectly viable. For both production run and weight of part, brightware parts lie happily within the range of possibility of die casting.

Die casting does have a variety of drawbacks. As already mentioned, the initial investment cost for dies and tooling is very large. This is coupled with the fact that the manufacture of dies is time consuming. The overall effect is that to make any changes to design or construct a prototype is expensive and takes a lot of time [23]. Parts manufactured using the process of die casting are susceptible to a variety of defects. As castings cool, they shrink. The amount of shrinkage will be dependent on the alloy amongst other factors. This can cause shrinkage porosity and or tears in the part [45]. The quality of the melt and correct filling of the mould are important in reducing the chance of defects occurring.

2.2.3 High Pressure Die Casting

High pressure die casting is variation from the die casting technique where molten metal is forced in to the mould under great pressure, instead of the force of gravity. The amount of pressure used is commonly of the order of 1000 atm [45]. The use of pressure increases the production rate but also increases the initial costs [23]. High pressure die casting, can be utilised for

high production of complicated designs with thin walls and high dimensional accuracy [42]. This ability to guarantee thin walls and section thicknesses is useful for brightware components and probably a factor in why the parts are currently manufactured like this. In summary, HPDC offers better productivity and the possibility for more intricate castings to be designed but this is counter balanced by the higher initial start-up costs.

Another downside of this technique is internal porosity from entrapped gas in the part. As the melt is injected under such high pressure it is easy for air to become entrapped within the part, which reduces the mechanical performance. In addition, if porosity not evenly distributed there will be a large variation mechanical performance across the part [42]. Porosity can also lead to problems in extreme temperatures as entrapped gas can expand and lead blistering at very high temperatures [46]. However, the negative factors of porosity should not necessarily be a major issue for the application of brightware parts as components should not be subjected to particularly large mechanical forces or very high extreme temperatures. That understood, it is important to appreciate possible flaws and problems with the manufacturing method, in order to avoid any unforeseen complications at a later date. By adding a vacuum degassing stage in the HPDC process, the porosity of the part can be decreased [42].

Approximately 80% of cast aluminium and magnesium alloy parts are manufactured using HPDC [46]. HPDC of Mg-Al alloys may lead to enhanced properties. For these alloys, the eutectic is divorced with a $Mg_{17}Al_{12}$ layer between the two alloys [46]. This layer improves corrosion resistance and is enhanced by more grain refinement. Zirconium can also be used as a grain refinement for Mg alloys but HPDC also leads to a finer grain morphology, so it is preferable to improve the corrosion resistance of these alloys [46]. HPDC is also an attractive manufacturing route for aluminium alloys. The automotive industry has driven a large rise in the complexity and quality of HPDC parts since the 1990s [47]. This led to a decrease in minimum wall thickness but larger overall parts. The typical surface finish for HPDC is better than for die casting. A typical value in surface roughness for parts could lie between 0.4 to 3.2 μm Ra [43]. The dimensional tolerances of the process are shown in the figure below.

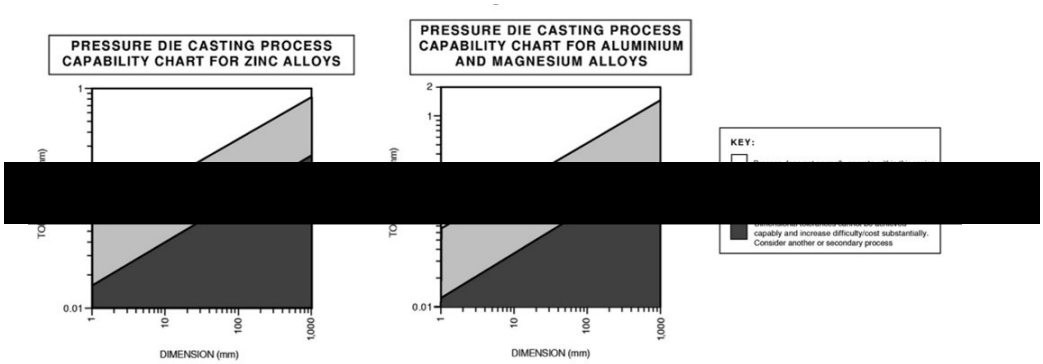

Figure 2.3: Representative tolerances for HPDC [43]

2.2.4 Metal Injection Moulding

Metal injection moulding is a process for producing large amounts of small parts with high geometric complexities and low dimensional tolerances. There is very low material wastage for the process which makes it competitive economically with other manufacturing routes [40]. Production rates range from 10-60 parts per minute with a production volume of 10,000+ parts per year needed to make the process economical [43]. This number will of course be dependent on the part being being produced but is possibly slightly higher than the production volume required for brightware.

MIM works by mixing metal powder with a binder and injected, using an injection moulding machine, in to a mould. The binder is then de-bonded, and the part is sintered. Binder may make up 40-50% of the feedstock but is necessary to allow the metal powder a molten body to be evenly dispersed and contained in the part [48]. The combination of space left by binder and subsequent sintering results in a size reduction of 12-18% [48]. This reduction is consistent across the part so it can be accounted for with careful mould design. The final density of the part is between 95-99% of the parent material [43].

During binder debonding it is possible for parts of the binder to react with the metal powder. This is especially prevalent with titanium that has a high affinity for oxygen and carbon that can be readily accommodated within interstitial lattice voids [48]. Porosity of the part negatively affects mechanical properties, especially fatigue resistance. Voids left from sintering allow cracks to initiate from these sites. Powder feedstock is vitally important in

the control of metal injection moulding. The powder size and morphology must be carefully monitored for effective sintering. The powder size can be up to 45μm but ideally the accepted sizes are much smaller [49]. Smaller particles allow for a rapid and more effective sintering. Care must also be taken within the mixing stage, so that agglomeration of particles doesn't occur and the distribution of particles sizes is not too large. Spherical particles are also preferred for a higher packing density [49].

The size and design of MIM parts that can be manufactured is limited by the process. The sintering rate needs to be roughly even through the whole part. Thick-walled parts will inhibit this and therefore, there is a natural maximum section thickness of around 12mm [43]. In addition, section changes from thick to thin should be gradual. This shouldn't be a particular concern for brightware parts, as they are normally designed with consistently low section thicknesses to reduce materials usage and part weight. The set up cost for MIM is quite high but this is offset by the rate of production which can keep the cost per part very low. Existing brightware parts are designed with consistent width walls which shouldn't cause problems for MIM. However, the size of some brightware parts may be very difficult to manufacture using MIM.

There are a variety of metals that can be processed using MIM. 80% of MIM products use steel and stainless-steel powders [50]. Of the light alloys that are available, titanium alloys are widely established for MIM [40]. In addition to titanium alloys, some research has also been conducted in to magnesium alloys for MIM [51]. This MIM of magnesium requires the use of specialist binder and a solution pre-treatment to remove the oxide layer from magnesium powder. Although in theory the use of magnesium is possible, established techniques with a defined supplier base would be necessary to implement the mass production of brightware. Therefore, the only material option available which would provide significant lightweighting for brightware is titanium. From the material review already conducted, it was clear that titanium would not be the optimum material choice for this application.

Metal injection moulding sees large use within the automotive sector. Globally the automotive sector is the second biggest market for MIM parts in terms of sales [50]. Typically, MIM parts for automotive applications include turbocharger components and fuel injectors. However, the process is also used for parts such as small knobs and levers, more typical of brightware parts.

One possible benefit of the technique is the possibility for creating a controlled level of porosity. Porosity is created by using a space holder in the powder mix. When this space holder is removed high levels of porosity of 65% are achievable [52]. Many space holders undergo thermal de-bonding which make them unsuitable for the sintering stage of MIM. NaCl and KCl can be used and de-bonded by simply dissolving them in water. The high level of porosity obviously reduces the weight of the part and is of importance to the medical implant field. This is relevant to brightware as it is possible to create very lightweight parts, due to the presence of voids within them. This comes with a decrease to mechanical performance but the level of mechanical performance can be tailored to the application, by increasing or decreasing the amount of voids in the structure. The problem with this porosity is that is equally distributed across the part and surface. This is incredibly useful for medical implants as it allows for bone and tissue growth to occur within the implant and provide a stronger connection between the body and material [52]. For the application of brightware though, the surface finish of the part is critical and having an open porous network for a part is not acceptable.

The process of metal injection moulding may not be viable for brightware parts for a variety of reasons. The maximum size of the parts is smaller than for castings, so the full range of parts may not be possible [53]. The other is the limited variety of powders available for manufacture. The aim of the project is to investigate lightweight alternatives to cast zinc alloys. However, all the major alloys used in metal injection moulding do not provide a significant weight advantage, apart from titanium. Titanium, however, does come with a large increase in the cost of material. Novel weight saving techniques involving using a space holder are also not suitable due to their poor surface finish.

2.2.5 Additive Manufacture

Casting and MIM create a solid homogeneous part. Small porosity may occur from air entrapment in HPDC, and MIM may result in some small porosity across the part. Normally, these voids would be undesirable in a part but for weight saving they could be utilised for greater gains. Parts with significant and intentional voids within them could reveal dramatic weight savings for parts. General Electric ran an open design competition in 2013 where people where challenged to redesign one of their brackets to reduce the weight as much as possible [54]. The new part design had to be capable to deal with

all the existing stresses that the current bracket was subjected to, which was tested using computer modelling during judging. The winning bracket was a design that reduced the weight of the part by nearly 84%, by utilising the capabilities of additive manufacture.

Additive layer manufacture involves the construction of parts by selectively melting or sintering individual layers of metal powder. These layers are then built up on top of each other. The process allows for net shape construction of very intricate patterns that other manufacturing methods would struggle or could not form [55]. Instead of machining a solid block of material, cavities or honeycomb internal structures can be built in to the design. This allows for some massive weight reductions for parts.

ALM techniques for processing metals fit in to two categories, powder bed fusion and directed energy deposition [56]. Powder bed fusion methods involve a heat source melting or sintering a pattern across a bed of metal powder. The powder bed is then lowered and more powder is added on top. Any excess powder is recycled. Every time the stage is lowered another pattern is melted and the layers build up to create the overall part. The power source could be a laser or an electron beam. Electron beams are much more powerful so they can process higher melting point metals, such as titanium. However, they also require a vacuum within the build chamber and are generally more expensive [56]. Direct metal deposition only deposits metal at the area to be melted, which can be in the form of powder or wire. As with powder bed fusion techniques, layers are built up sequentially. Wire based additive manufactured parts melt a spool of wire while running it over the area to be covered. This has a much higher production rate than other processes but the level of detail is much lower. Alternatively, powder can be distributed next to the heat source using a nozzle [56].

As well as massive possible weight reduction AM has several other benefits. There is a very high utilisation rate which means less material wastage. The initial cost of manufacture is kept low as there is no need to machine expensive dies. Near net shapes are manufactured which require less machining. Skilled operators for the manufacturing process are also not required as the machine can be left to build the part itself [55]. These are all cost factors which make AM more attractive as technique.

The build times for additive manufacture are part dependent on part size. However, they are more likely to be in the region of hours not minutes. Coupled with the high cost of running the power source makes AM currently

unsuitable for high production runs [57]. As mentioned earlier in this review, Aston Martin are looking at manufacturing thousands of similar parts. An alternative method of die casting can become economically equivalent with ALM for a surprisingly low number of parts. One cost analysis for a part showed that the breakeven point for ALM and HPDC was only 42 parts [57]. The economics of a process are obviously going to be very dependent a variety of factors but the point remains that ALM techniques are not usually viable for large scale production. One way that ALM methods can become cost effective is by making savings while in service. The cost of producing a single ALM part remains constant while the cost of a HPDC part drops at a decreasing rate with an increase in production volume. It may only take 42 parts for a HPDC parts to become cheaper per part but the decrease in cost after that point, while substantial, is not as major as the initial fall. Studies on the savings of ALM parts have shown that 40% weight reductions are easily possible with redesign and that a decrease of 100kg leads to savings of 770 euros per car [58]. This is a saving in fuel for the customer though and not a saving in production for the manufacturer. Therefore, unless Aston Martin are feeling incredibly charitable, the economics still don't appear to make sense.

The other major drawback of ALM parts for this project is their poor surface finish. Various process parameters, powder characteristics, and other defects such as porosity can increase the surface roughness. The inherent surface roughness is dependent on the fact that the curved edges of the part must be made up using straight lines of powder [56]. In addition, any un-melted or poorly fused powder will create a balling affect, increasing the surface roughness. Extra processing steps to remedy this would incur an extra cost in manufacture. Good surface finish is a key requirement of brightware.

2.2.6 Semi Solid Metal Casting

Thixo/Rheoprocessing routes are examples of semi solid metal forming techniques. These techniques utilise a microstructural change in the molten metal, to increase the fluidity of the casting. There are many potential benefits of adopting this approach. These include less shrinkage of the casting, as it is solidifying from a semi solid state, not liquid. Secondly, there is less turbulence in the melt when filling a die which has many positive effects. There is less air entrapment that could lead to defects within the part that would contribute to inferior mechanical properties. Smooth filling also leads

to a good surface quality and thin-walled sections of high integrity [59].

Both techniques rely on transforming the microstructure of the while it is the semi solid region between the liquidus and solidus. The aim is to break up the solidifying dendritic structure in to a globular microstructure by applying a large and constant shear force. This reduces the viscosity by nearly three orders of magnitude [60]. 30-50% of the melt will be retained in the liquid state for processing while the globular microstructure doesn't inhibit the flow of the metal by entangling like the dendritic structure would.

Thixo based routes involve reheating ingots or billets of previously transformed Semi-Solid Metal. These billets are reheated to the Mushy Zone and then formed via a variety of techniques. Thixo routes allows Semi-Solid Metal material to be transported between to different locations for processing. It also means that billets can be processed in a variety of different routes such a thixo-forging and thixo-casting. Rheocasting involves putting the melt straight in to a die after the semi solid metal processing. This way less time is spent processing and there is need and therefore cost for reheating the Semi-Solid Metal.

There are multiple ways of creating an appropriate semi-solid slurry. The simplest way to achieve a slurry is to use a mechanical stirrer. However, this can cause surface disruption which is undesirable. Other techniques can involve using selective nucleation and heat treatments to promote the globular microstructure [60].

Traditional casting alloys have a very low freezing range to avoid defects, such as cold shuts. For Semi-Solid Metal a large freezing range is needed for a large mushy zone to modify the microstructure in. Therefore, the alloys used for Semi-Solid Metal are often more specialised and expensive [60]. In relation to brightware parts, Semi-Solid Metal processing allows for highly complex and thin walled shapes which is relevant to the application. The high integrity of parts isn't necessary for brightware parts and the higher cost of specialised feedstock alloys is not a positive.

2.2.7 Metal Foams

Metal foams can be grouped in to open and closed cell structures. For this review, the closed cell structures will be focused on. Open cell structures have interconnected pores which is more useful for biomedical applications

and as heat exchangers [61]. They have an open porous surface which allows air to permeate cleanly through the structure. This is not preferable for a brightware application where surface finish is key.

The properties of metal foams are attractive to the automotive and aerospace industries. They have a low weight due to their high porosity, but they also have good specific strength. The other unique benefit of metal foams is that the mechanical properties are highly tailorable by varying the pores and density of the foam [61]. This means that the density can be reduced to a minimum, depending on the application of the part.

Materials that have the potential to form metal forms include: Aluminium, Titanium, Magnesium, Stainless Steel 316 and Zinc [62]. Aluminium foam sandwiched between aluminium sheets is also an option for structural panels to obtain a better surface appearance. Internal 3D geometries are in direct competition with sandwich panels and have been shown to have a greater weight saving as a designer can choose where and where not to locate material. However, metallic foams are generally easier to manufacture and have better acoustic and heat resistant properties [61]. Car manufacturers are beginning to experiment with sandwich panels for larger flat shape geometries. The impact resistance of these sandwich panels has been found to be suitable for use on vehicles [63]. This could provide opportunities for part redesign using less material that would make aluminium foams more economically viable. Brightware parts are currently designed with minimal wall thicknesses and to accommodate pores with the structure may not be possible based purely on the basis that there isn't the space to hide the porosity with such thin walls.

Chapter 3

Cast Aluminium

The initial literature review outlines a variety of possibilities that could be used for light weighting of brightware. Some of these approaches are more appropriate than others. This will be summarised in more detail within the discussion section of this thesis. It was decided that further investigation should be conducted on of cast aluminium alloys for this application. The decision was made by balancing the potential for weight savings against whether the demands of the application could be achieved. Cast aluminium parts offered a realistic chance of creating lighter parts, that also satisfied the demands on mechanical performance and corrosion resistance. Magnesium alloys would have provided greater weight saving potential but their corrosion resistance, especially on the outside of the vehicle was a concern. Other manufacturing techniques, such as additive manufacture, could have provided a large weight saving. However, an appropriate decorative surface finish would have been difficult to achieve.

Once cast aluminium had been selected, more research was necessary to narrow down which cast aluminium alloys might be relevant for use in brightware parts. There are a large variety of different aluminium alloys based on a range of alloy systems. Due to the large range of options, there is a large range of suitability for these alloys to brightware parts. Many alloys are instantly unsuitable as they are only cast by expendable mould techniques. This would not provide the production volumes or dimensional quality required. Different alloy systems and alloys within them will be summarised in the following section. This should outline the qualities of these different alloy systems and their limitations. The aim is that this will lead to a summary about which alloys are most suited to the application of

brightware.

The current brightware parts used by Aston Martin are designed with minimal section thicknesses to reduce the weight of the part. The zinc alloys that are currently used to cast brightware parts have very good castability. If an alternative aluminium alloy was used to cast brightware parts and the castability was lower, then the section thickness may be increased. More material being used would result in a heavier part. Therefore, the castability of the part is important for the weight saving potential. The other major consideration for aluminium alloys is the surface finish possible. Obviously, for brightware components the aesthetic appearance of the part is very important. Anodised surface finishes are of interest for Aston Martin, as they would allow dyeing for a wide variety of colours. The quality of any anodised finish is therefore very important to brightware parts.

The three aluminium alloy systems chosen for further investigation were the Al-Zn, Al-Mg and Al-Si alloys. Al-Si was chosen as these alloys are the most castable. The remaining two systems were chosen as they apparently provide the best potential for decorative anodising.

3.1 Cast Aluminium Alloy Systems

3.1.1 Aluminium-Silicon 3xx Series Alloys

Aluminium-Silicon alloys are the most widely used aluminium alloys for casting. They fall under the designation of the 3xx.x series (silicon and/or copper and magnesium) and 4xx.x (silicon) series alloys. Copper and magnesium are both widely added to Al-Si alloys for enhanced properties. Copper improves strengthening and machinability, while magnesium additions give alloys an excellent balance between castability and performance after heat treatment [22]. The corrosion resistance of Al-Si-Mg alloys is also very high, whereas an increase in copper content negatively affects the corrosion resistance of aluminium alloys [22].

Silicon has a very large impact on the fluidity of aluminium alloys. As an impurity silicon would be expected to reduce the fluidity of aluminium alloys [64]. However, the castability of Al-Si alloys is superior to other cast aluminium alloys. Silicon has a latent heat of solidification 4.65 times greater

than aluminium [65]. This extra heat is put back in to the alloy during solidification, increasing the fluidity during solidification. Therefore, the proportion of silicon is important to determine the fluidity of aluminium alloys.

Table 3.1: The composition of some common Al-Si casting alloys [22]

Alloy	Composition wt% (limits)										
	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Sn	Others	Al
356.0	6.5-7.5	0.6	0.25	0.35	0.20-0.45	-	0.35	0.25	-	0.15	Bal
380.0	7.5-9.5	2.0	3.0-4.0	0.50	0.10	0.50	3.0	-	0.35	0.50	Bal
383.0	9.5-11.5	1.3	2.0-3.0	0.50	0.10	0.30	3.0	-	0.15	0.50	Bal
413.0	11.0-13.0	2.0	1.0	0.35	0.10	0.50	0.50	-	0.15	0.25	Bal

The majority of Al-Si alloys that are cast, are hypoeutectic alloys. This includes the ones selected in table 3.1. Silicon has a low solubility in aluminium so it can't all be contained within a eutectic phase. The solidified microstructure of a binary Al-Si alloy consists of a eutectic of an aluminium solid solution, with around 1wt% silicon and a almost pure silicon second phase [18]. This is contained within an aluminium matrix.

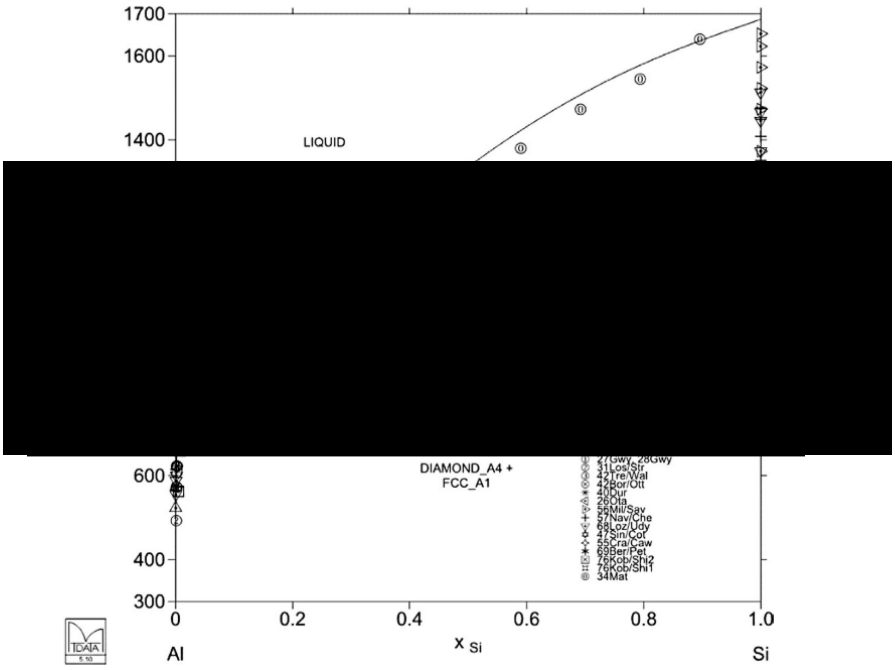

Figure 3.1: The binary phase diagram for the Al-Si system [19]

Silicon takes the form of flakes within the microstructure and is interconnected within the eutectic. The eutectic can be modified using strontium as a grain refiner. Strontium changes the morphology of silicon in the microstructure from course acicular, to a fine fibrous structure [66]. This provides a more even distribution of the silicon 2nd phase in the microstructure.

Table 3.2: The mechanical properties of some common Al-Si casting alloys [22]

Casting technique*	Alloy	Density (g/cm^3)	Melting range (°C)	UTS (MPa)	YS (MPa)	Hardness (HB)
Gravity	A356.F	2.67	560-610	275.79	206.84	75
Die	A380.F	2.71	540-595	324.05	158.60	80
Die	A383.F	2.74	516-582	310.26	151.68	75
Die	A413.F	2.66	574-582	296.47	144.79	80

3.1.2 Aluminium-Magnesium 5xx Series Alloys

Cast Al-Mg alloys come under the designation 5xx.x for cast alloys under the North America Aluminium Association Inc designation system. The standout strength of these alloys compared with other aluminium alloy systems is their resistance to corrosion [18]. The use of wrought Al-Mg alloys for structural purposes is limited by the fact these alloys can't undergo an ageing procedure to increase their strength. Some investigation has been conducted on adding silver to these alloys to promote a response to precipitation hardening. It has been reported by C. Guo and other that addition of silver to Al-Mg alloys can promote an age hardening response and improve the intergranular corrosion [67]. The castability of Al-Mg alloys is not as good as the Al-Si alloys, so special care needs to be taken with mould design to achieve a defect free casting. Beryllium can be added in small amounts to the melt to reduce oxidation during casting, but this can result in the formation of the toxic BeO [18].

Table 3.3: The composition of some common Al-Mg casting alloys [22]

Alloy	Composition wt% (limits)										
	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Sn	Others	Al
513	0.30	0.40	0.10	0.30	3.5-4.5	-	1.4-2.2	0.20	-	0.15	Bal
514	0.35	0.50	0.15	0.35	3.5-4.5	-	0.15	0.25	-	0.15	Bal
518	0.35	1.8	0.25	0.35	7.5-8.5	0.15	0.15	-	0.15	0.25	Bal

The phase diagram for binary Al-Mg alloys shows that, at similar compositions to the alloys in table 3.3, a eutectic of Al and β phase (Al_3Mg_2) will be present. This eutectic transformation occurs at 450°C [19]. Scandium can be added to cast Al-Mg alloys as a grain refiner. Casting Al-Mg alloys with

5wt% Mg have a dendritic microstructure within coarse grains of Al phase. At 0.4wt% Sc addition, the average grain size is reduced, and the dendritic microstructure is refined in to an equiaxed grain structure. This also results in an increase in tensile strength, yield strength and hardness for a reduction in ductility [68].

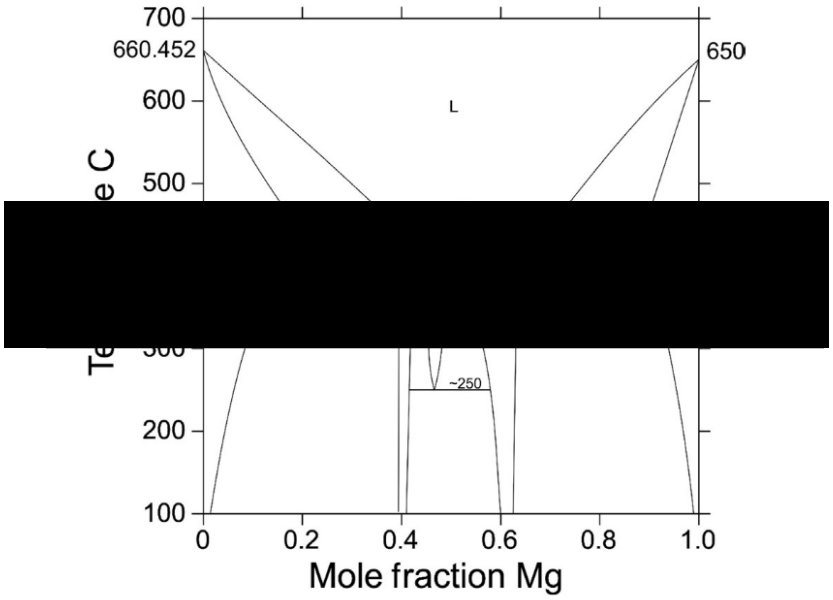

Figure 3.2: The binary phase diagram for the Al-Mg system [19]

Table 3.4: The mechanical properties of some common Al-Mg casting alloys [22]

Casting technique*	Alloy	Density (g/cm^3)	Melting range (°C)	UTS (MPa)	YS (MPa)	Hardness (HB)
Gravity	A513.F	2.68	580-640	186.16	110.32	60
Sand	A514.F/LM5	2.65	600-640	172.37	82.74	50
Die	A518.F/LM10	2.57	535-621	310.26	193.05	80

3.1.3 Aluminium Zinc 7xx Series Alloys

Cast aluminium-zinc alloy have the American alloy designation of 7xx.x series alloys. Wrought Al-Zn alloys are used within the aerospace sector for their balance of strength and toughness [69]. Cast aluminium-zinc alloys are less popular but are used as sacrificial anodes to protect marine structures [18]. Hot cracking of Al-Zn alloys can be problematic with permanent moulds, so sand casting is more popular for these alloys [70]. This would be problematic

for the production of brightware parts which requires a permanent mould technique for the production volumes to be economically viable.

These alloys age at room temperature over time over a period of a couple of weeks [18]. Zinc has a very large solubility in aluminium. So much so that zinc and aluminium do not form intermetallic phases within each other [71]. The microstructure consists of a solid solution of aluminium and zinc. At equilibrium, a casting alloy will contain a α-phase of almost pure aluminium that forms a matrix and a β-phase of almost pure zinc [71]. Depending on the cooling rate and composition of the alloy a supersaturated solid solution will be formed at room temperature. This microstructure will undergo ageing at room temperature. Gunier-preston zones are formed which will eventually decompose in to the β-phase. This transition can have multiple steps or happen in one go, depending on the original size of the particles. This decomposition at room-temperature leads to a reduction in strength of castings during the first few weeks.

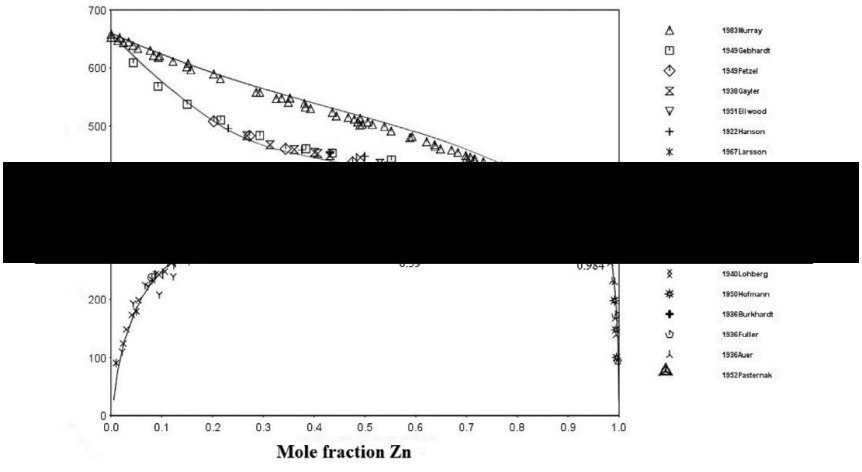

Figure 3.3: The binary phase diagram for the Al-Zn system [19]

Common cast aluminium alloys have a zinc content of around 5-8wt%. However, investigation has been completed on Al-Zn alloys with much higher zinc content for use as cast alloys [69][72]. These alloys contain zinc contents of 20wt% and above. As the zinc content is increased, the solidus temperature drops, which in turn improves fluidity. Alloys with 30wt% zinc have demonstrated greater fluidity than aluminium silicon alloys such as A380 (equivalent alloy) [69]. In addition, alloys containing 15-30wt% Zn display good strength and dampening properties [72].

This investigation is focusing on Al-Zn alloys with a lower zinc content than newly designed alloys for die casting. This is as the aim of the investigation is to look at possible alternative materials and manufacturing solutions to automotive, that could be implemented right now. It would be difficult to test and implement a material that is currently in the development stage, as the proper supply chains and manufacturing knowledge for this material would not have had chance to develop. Therefore, although hyper-eutectic zinc alloys show some interesting properties, they are not yet relevant.

Table 3.5: The composition of some common Al-Zn casting alloys [22]

Alloy	Composition wt% (limits)									
	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	Others	Al
711	0.30	0.7-1.4	0.35-0.65	0.05	0.25-0.45	-	6.0-7.0	0.20	0.15	Bal
712	0.30	0.50	0.25	0.10	0.50-0.65	-	5.0-6.5	0.15-0.25	0.20	Bal
713	0.25	1.1	0.40-1.0	0.6	0.20-0.50	0.15	7.0-8.0	0.25	0.25	Bal

The addition of cerium to Al-Zn alloys as an addition, has been investigated [73]. The aim of this is to increase the strength of these alloys as cerium can form various eutectics in other aluminium alloy systems. The strength of binary Al-Zn alloys was increased by the addition of small amounts of cerium [73]. This could be used to counteract the reduction in strength from the decomposition.

Table 3.6: The mechanical properties of some common Al-Zn casting alloys [22]

Casting technique*	Alloy	Density (g/cm^3)	Melting range (°C)	UTS (MPa)	YS (MPa)	Hardness (HB)
Gravity	711.0	2.84	600-645	193.05	124.11	55-85
Sand	712/LM31	2.81	600-640	234.42	172.37	60-90
Sand	713	2.81	595-630	220.63	151.68	60-90

3.2 Relative Fluidity of Cast Aluminium

The castability of an alloy is a qualitative term to describe how well a particular alloy can be cast in to shapes to produce sound castings [74]. There are multiple elements which combine to create the castability including the filling characteristics of the melt, the ease of casting and the tendency for cast parts to be rejected. Filling characteristics would include the fluidity of the melt and the minimum section thickness possible. Ease of casting could include the energy needed to produce a part and the tendency for die soldering. Rejection of parts is due to phenomena such as hot cracking and misruns. As castability is a qualitative term it is difficult to compare between alloys.

Fluidity is a key element of the castability of an alloy. Whereas castability is a broad term that can be described qualitatively, fluidity is a more narrowly defined term that can be measured quantitatively. Fluidity can be expressed simply as the distance which a metal will run through a mould [8]. For this report when comparing castability, the fluidity of relative alloys will be key. That is not to say other aspects of castability are not important. However, the more fluid a metal is, the easier it is to cast in thin sections as seen with brightware. Therefore, this study will focus on fluidity as it offers quantitative values, which provide a better comparison between alloys and are highly relevant to brightware parts.

The aim of reducing the weight of brightware parts is fundamental to the project. To achieve this, casting parts with low section thickness is a sensible approach. Currently, the cast zinc used, is cast with very thin walls. This lowers the weight of the part while also reducing the material cost of each part. Therefore, for an aluminium alternative to be competitive, the castability needs to be great enough as to not negate the positive impact of the less dense material. Below is a thickness analysis on a 3D model of an existing cast zinc part. This shows an average part thickness of around 2mm across the whole part but some fins on the underside of the part go as low as 1mm thickness.

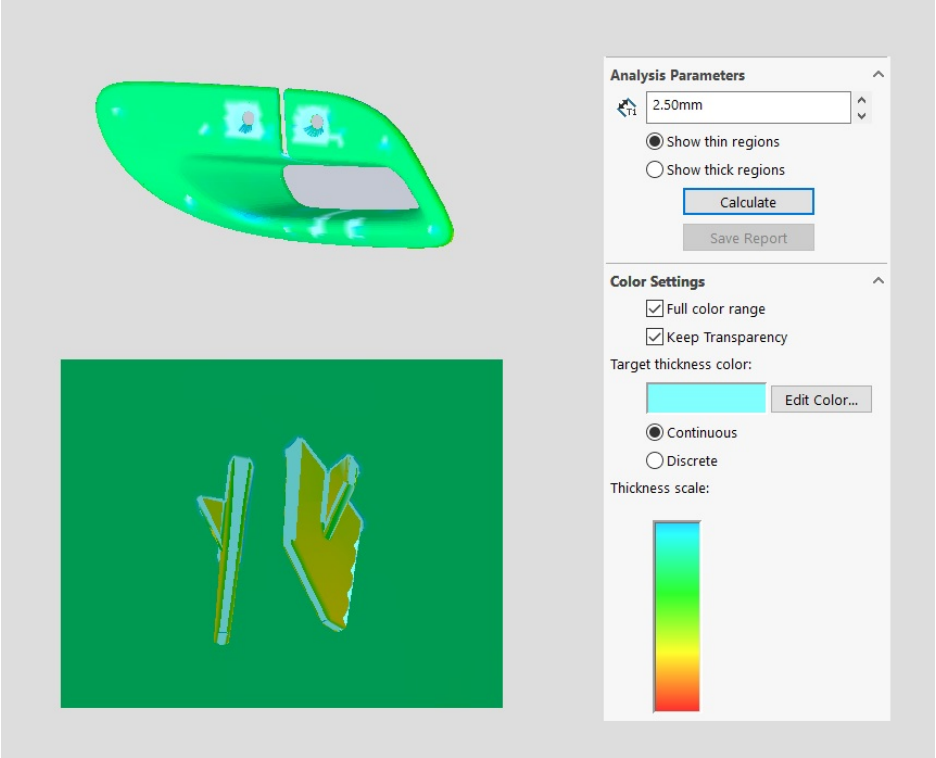

Figure 3.4: Thickness analysis of an existing cast zinc part

There are a variety of different fluidity tests and there many variations that can considered within these tests. The traditional fluidity test is the spiral fluidity test. This involves pouring a melt through a spiral shaped mould and judging the fluidity based on the distance around the spiral that metal reaches. The benefits of a spiral test are that the mould takes up less space instead of casting a single large strip. The distance that the melt will flow is also sensitive to how level the mould is kept. If the mould is a spiral, then the levelling errors should cancel each other out [75]. The downsides to the spiral fluidity test are that it can be difficult to equate the data to real world casting applications. It can be difficult to relate how metal flows through a spiral of a set cross section to how it will flow through a mould of a completely different and varying cross section. The strip fluidity test aims to help resolve this by filling strips of different cross section from a single runner section [76]. Other fluidity tests include the vacuum tube fluidity test, where a chamber is depressurised using a vacuum pump. The force from the vacuum in this chamber is used to draw metal up a tube. The distance up the tube that the metal travels gives the fluidity of the metal.

All these tests involve measuring the distance that metal can flow down a section before stopping.

Although fluidity tests give a numerical value it is sometimes difficult or inappropriate to compare directly between results. This is as there are many variations within the strip and spiral fluidity tests. This includes: the gating and channel thickness of the mould, whether the mould is closed or open, the pressure applied to the metal, the amount of superheat in the melt, what material the mould is made from and more [74]. Where possible the report will focus on the difference in fluidity between alloys under the same test conditions. However, When comparing between different tests, the differences in characteristics between the tests should be considered and their predicted effect explained.

3.2.1 Comparative

Originally, the plan to test castability had been to cast representative parts with thin wall sections in useful Al-Si, Al-Mg and Al-Zn alloys. This would have allowed the castability of each possible alloy system to be compared. Unfortunately, due to cost and time factors this approach was not possible. Therefore, a separate review on the fluidity of all the possible alloy systems was completed. As already seen, brightware parts are designed with minimal section thicknesses of around 2mm. Part size varies a large amount but the large strake pieces can be around 40cm long. For there to be no concerns about fluidity, fluidity lengths in the literature should ideally be around 40-50cm long or greater and cast in thin sections.

G.Lang studied the varying the fluidities of a large variety of binary aluminium alloy systems over a large compositional range and at a variety of pouring temperatures [77]. This study included the binary Al-Si, Al-Mg and Al-Zn alloys, the alloy systems being considered for use in the application of lightweight brightware.

For the binary Al-Si system, at 700 °C, the spiral fluidity was recorded at just under 40cm for the pure alloy with no additions. Fluidity falls to a minimum of around 12cm, at around 3wt% silicon. The fluidity then rises again as the freezing range decreases towards the eutectic point at 12wt%. Past the eutectic point the fluidity increases towards 18wt%, where it peaks at roughly 42cm [77]. The fluidity of Binary Al-Zn alloys starts at the same point as that of Al-Si alloys for a pure system. This is expected as this is the

same pure aluminium alloy. The fluidity then more than halves to around 17-18cm at 5wt% and continues to fall a minimum of 15cm at 13wt% zinc. The fluidity then rises slowly from this point [77]. For binary Al-Mg alloys the initial fluidity drops far more rapidly than for the other alloy systems. The minimum fluidity of 15cm occurs at approximately 3-4wt% and then rises relatively linearly. The fluidity is around 24cm at 15wt% Mg [77]. Al-Zn alloys, such as 711 and 713, and Al-Mg, such as 518, don't contain more than 8wt% of the main alloying element as a maximum and most contain closer to 5wt% [22]. For this wt% of main alloying element, both binary systems display fluidity values around 15-16cm. Alternatively, aluminium silicon alloys such as A380 and A383 will reach 10wt% and higher silicon content. This would result in a fluidity for a binary system of over 20cm. All the alloys demonstrated an initial fall in fluidity to minimum points, which were all similar values of fluidity. However, this minimum fluidity point is much closer to typical Al-Mg and Al-Zn casting alloys than Al-Si alloys. In addition, the Al-Si phase diagram shows a much larger increase in fluidity, once the minimum point has been passed. Therefore, the potential for Al-Si alloys to provide large fluidity values appears to be much greater.

In general, as the wt% of the alloying element increases, the fluidity suddenly drops. This reaches a minimum before rising again to the eutectic point. The exception to this rule is the Al-Si system, where fluidity rises past the eutectic point. The fluidity would be expected to peak at the eutectic point as the solidification range is lowest here. The increase of fluidity past the eutectic point is attributed the very high latent heat of fusion for silicon, which prolongs the solidification process and increases the fluidity of the alloy [18].

Most modern alloys and the alloys that are of interest to this investigation are not simple binary casting alloys. However, even for complex alloy systems, the two main alloying elements will dominant the system in wt%. Binary alloys give the opportunity to study the general trends of casting alloys and relative fluidities. Small additions may be capable of grain refinement, enhancing fluidity or increasing the ageing response. However, the scale of these changes will be limited by the small wt% of their use, so binary alloy systems are an okay starting point for the overall characteristics of the alloy system and fluidity. This test is limited by the fact that all the systems were tested at 700°C pouring temperature. Although the same temperature, this will not equate to the same superheat.

If Al-Si alloys are the most castable, then it makes sense to evaluate their

fluidity performance as a benchmark for the other alloys. Prukkanon et al. investigated how modification of Al-Si alloy A356 affected its fluidity [78]. The method used was a vacuum pipe fluidity test where the pipe had an internal diameter of 7mm. This equates to a cross sectional area of just under 40mm^2. This is slightly larger than the minimum cross section for a brightware part. The fluidity of the alloy was found to be 45cm when tested at 690°C and scandium addition was found to have no noticeable effect on the fluidity of the melt. Scandium did have a grain refinement effect on the microstructure. The fluidity of 45cm is around the length of the large strake parts. However, the diameter of the pouring channel in this fluidity test is larger than the section thickness in the current parts used.

Eisuke , Koichi , Tatsuya and Sadato completed similar testing on an AC4CH alloy, which is an equivalent composition to the A356 alloy [79]. The diameter of the tubes used was much smaller than for the previous experiment and possibly more representative of brightware parts. For the same tube material of quartz and a similar pressure of 67kPa, the fluidity of A356 in a 3.5mm diameter tube was just over 75mm. This is significantly less than the 450mm for a tube of twice the internal diameter in the Prukkanon test. Eisuke.et al [79] found a linear relationship between fluidity and tube diameter. Argon de-gassing and mould coating were both also found to have a positive impact on the fluidity. This testing showed that when the section thickness was decreased to to close to that of the current part thickness, the fluidity recorded showed a large decrease to values that were not useful for large brightware parts.

Han Q and Xu H tested the fluidity of a variety of common commercial aluminium silicon alloys [80]. These alloys were tested in a ragone test which is similar to the quartz vacuum tube test, and then under pressure die casting conditions. The maximum values for fluidity were higher for the A380 alloy than the A356 alloy. When these alloys were tested using pressure die casting, the fluidity of the samples increased dramatically. The mould channel used had a cross section of 1mm x 15mm which is similar or maybe slightly thinner than you would expect for a brightware part. Both the alloys A380 and A356 demonstrated fluidity values scattered between 480-600mm. This range of fluidity lies around the sort of values that are necessary for the larger brightware parts and is more than adequate for the values necessary for the smaller bezel parts. It is also reasonable to expect that any values of fluidity would be greater if a 2mm section thickness had been used. Therefore, fluidity measurements from pressure die casting at section thicknesses of 1mm (below the standard part thickness) for Al-Si alloys, appear to be suitable

for all brightware parts.

The work of G.Lang [77] has shown that for binary systems the fluidity of Al-Si shows more potential than the other two systems for casting intricate and thin wall sections. Research from Srisukhumbowornchai and Limmaneevichitr and Eisuke et. al investigated the fluidity of Al-Si alloys under conditions that are more similar to die casting than pressure die casting. Under these conditions, the fluidity of Al-Si alloys were slightly lower than what would be necessary for casting larger brightware parts. Han and Xu have shown the fluidity of pressure die cast Al-Si is right in the range of values that would be acceptable the largest brightware components. Consequently, the die casting characteristics of these alloys seems to be adequate for the application of brightware components. What remains to be seen is how appropriate the other alloy systems of Al-Mg and Al-Zn are to the application and what fluidities they may achieve. The next stage of this fluidity review is to compare the results of Al-Si alloys against values for Al-Mg and Al-Zn alloys.

Shin J et al. studied the castability of a new Al-Zn alloy for automotive applications [81]. The zinc content of this alloy is similar to the 711 and 712(LM31) casting alloys [81][22] but the magnesium content was higher to reduce the tendency of hot tearing. The fluidity tests completed were both spiral and strip tests, where the results were compared against A356. The cavity size for the spiral test was $40mm^2$ and channels in the strip test were 10mm x 1,2,4 and 8mm respectively. These range of values for the strip fluidity test are representative to some of the varying section thicknesses seen in brightware. The fluidity tests completed were spiral and strip in ceramic coated steel moulds. The superheat used was either 200°C or 100°C. Low pressure was used for the strip and gravity for the spiral tests. For the 1mm diameter test, fluidity of the Al-Zn alloy was around 18mm, and 74mm for the 2mm test. This compares with 20mm and 65mm for the A356 [81]. The spiral test showed that the fluidity length was around 60-70% lower than that of A356 for the new Al-Zn alloy. This still meant a recorded fluidity length of 450mm for the new Al-Zn alloy. This sort of result is good for the small brightware parts and close to the range of larger brightware parts. The fluidity for thin walls of 1mm and 2mm was also similar to the A356. This depended on finding the balance correct balance of magnesium and titanium addition, in order to optimise the fluidity. The average fluidity length in 2mm sections was greater for the Al-Zn alloy than the A356. As parts for brightware will have thin sections across the whole geometry. A fluidity length of 70mm for 2mm sections seems inadequate for

the application. However, the values of fluidity gathered for thin sections in this report are comparable with that of A356, which has already been seen to produce much greater fluidity lengths under pressure. It may be that this new alloy could also produce greater values for fluidity under high pressure casting conditions. However, this is just speculation until any testing is completed under high die casting conditions. Overall, the general fluidity appears to be lower than the Al-Si alloys but the thin section thickness may be comparable.

A.K. Birru et al. conducted testing on Al-Zn alloy A713 to record the effect that scrap addition had on the fluidity [82]. They found that a mould coating had a positive effect on fluidity. Whereas, an increase in scrap content had a negative effect. The maximum fluidity length for for a spiral mould test the area was 35cm down an approximately 40mm^2 channel [82]. This level of fluidity would be adequate for smaller brightware parts, if they also had larger section thicknesses. This maximum result also relied on optimisation of the pouring temperature, scrap level in the alloy and coating of the mould. When scrap was involved in the melt and no coating was applied, the value of fluidity in the same test decreased to only 19cm [82]. This value of fluidity is getting in to dangerous territory for the casting of smaller brightware parts and it is still using a larger section thickness/pouring channel.

The review of fluidity for Al-Zn alloys has shown that they can not compete with the fluidity of Al-Si alloys under die casting conditions. An example of a novel Al-Zn alloy did show comparable performance to Al-Si alloys when casting thin walls but still could not match their performance in spiral fluidity tests. The spiral fluidity of more common Al-Zn casting alloys was shown to be optimised to reach 35cm under die casting conditions. This would likely only work for smaller brightware parts and include redesigning them. Additionally, when you contrast the performance of Al-Zn alloys to Al-Si alloys that are pressure die casted. The difference in performance between the two is even larger.

The remaining aluminium alloy system for investigation is Al-Mg. Ravi KRR et al completed a review of the fluidity of aluminium alloys [64], which included Al-Mg alloys. During this review, the effect of mould and pouring temperature were also reported. This also showed that the fluidity of Al-Mg10% is less than Al-Si12%. The fluidity of the Al-Mg10% was about 75% of the Al-Si12% alloy across the range of mould temperatures tested. This is similar to the relative fluidity of Al-Zn to Al-Si as seen in the study by Shin J et.al [81].

Di Sabatino M, Arnberg L investigated the fluidity of different aluminium alloys using a commercial strip mould test [74]. A final value fluidity value was achieved by the addition of each of the individual lengths of strip. This gives an idea how fluid a metal is over a range of cross sections, a situation that will be more likely in casting an actual part. However, you lose information about thin wall fluidity as all the data is clumped together. This is unfortunate as information about casting thin sections is important for the application of lightweight automotive brightware. Aluminium A520, which has a magnesium content of 10% similar to the alloy tested by Ravi KRR et al, was compared against aluminium A356. The results gathered by this investigation showed that the fluidity length achieved by A520 was around 75% that of A356. This correlates with the findings of Ravi KRR et al and is a similar to the difference in fluidity of Al-Zn compared to Al-Si alloys, as found by Shin J et al. Al-Mg10% is a higher magnesium content than you would expect for some of the more common casting magnesium casting alloys [22].

So far the review of fluidity studies have shown that Al-Si alloys, such as A356 and A380, demonstrate superior fluidity to the Al-Zn and Al-Mg systems. The fluidtiy of Al-Zn alloys in thin sections has been comparable with some Al-Si alloys. The fluidity investigations of Al-Zn and Al-Mg alloys show similar results when compared against Al-Si alloys, such as aluminium A356. Alloys of both Al-Zn and Al-Mg demonstrate fluidity values of around 70-75% that of A356. The difference in the fluidity between Al-Zn and Al-Mg appears to be small, in order to recommend which alloy type has better fluidity, a comparison test of the two is necessary.

Birru, A.K. Mahapatra and M.M. Karunakar compared the fluidity of Al-Mg and Al-Zn alloy fluidity as well as comparing their propensity for hot cracking [70]. Spiral fluidity tests were conducted on Al-Mg alloy A518 and Al-Zn alloy A713. Testing conditions were reported as follows. A spiral mould in green sand. The section diameter was 1.27cm x 0.3175cm and the melt was poured at temperatures of 680°C, 715°C and 780°C. This channel thickness is around 40mm^2 and not as thin as brightware parts. For temperatures of 680°C and 715°C, the A518 alloy had a higher fluidity than the A713. At these temperatures the maximum fluidity of the Al-Zn alloy was only 15cm, which not acceptable for brightware parts. The Al-Mg alloy reached a fluidity length of 34.5cm at 715°C which is more appropriate for automotive brightware. The fluidity of Al-Zn was raised dramatically to 48cm at 780°C, which was higher than the 37cm for the A518 [70]. However, to minimise operating costs it will be important to reduce the heating of alloys

in a foundry as much as possible. So this result is less useful for a real world application. These comparative results also show that the fluidity of Al-Mg alloy was greater than the Al-Zn alloy tested. The hot tearing tendency of A713 was also much higher than that of A518. In fact, the Al-Mg alloy did not produce any hot tears in testing whereas there were multiple hot tears for the Al-Zn alloy.

Overall, this mini review has investigated fluidity to determine which aluminium alloy systems have potential to cast automotive brightware. The fluidity values of high pressure die cast aluminium-silicon alloys were shown to be in the range where they seem appropriate for all types of automotive brightware, both large and small. The fluidity of die cast aluminium-silicon alloys was lower than for pressure die cast systems and could present challenges for the larger brightware pieces. Al-Zn and Al-Mg alloys showed similar fludities, both lower than the Al-Si alloys by around 70%. Between these types of alloys, the Al-Mg appears to show better fluidity and lower hot cracking tendency. There are still significant worries over how well this alloy can be cast in to brightware parts. Greater tolerances are possible with high pressure die casting, rather than die casting techniques. Therefore, to reduce the section thickness and weight, ideally a pressure die casting technique would be better for automotive brightware. A company called Anodic Casting Ltd were successful apparently successful in mastering the use of Al-Mg alloy LM5, in a pressure die casting process [83]. Super pure primary ingots were required in order to allow proper anodising at a later stage. Casting size of 100g was the optimum to retain the tolerances of parts but 350g is an upper limit of what size of part was possible. Parts manufactured by these techniques included decorative components, such as handles and pipes.

3.3 Anodising Cast Aluminium

One of the possible benefits of using aluminium is that it can be anodised to produce a variety of finishes. This is not only limited to the traditional high gloss shiny finish that you may expect, but also dyed finishes in a variety of colours. This would be highly attractive to a designer as it would allow for a great degree of customisation throughout a car. Therefore, anodising potential of alloys is important for brightware. In addition, the corrosion and mechanical resistance of parts can be increased by anodising.

Wrought alloys are normally favoured for anodising over cast alloys to produce better quality results. Cast alloys will generally have a higher alloying content then wrought alloys. This is as wrought alloys aim to maximise ductility and formability, whereas cast alloys require a small freezing range for castablity. When anodising, it is only the aluminium that is needed to form the aluminum oxide layer. Wrought alloys are closer to pure aluminium, so there is a greater proportional supply of material to use in forming an oxide layer. In addition, porosity and foreign agents such as lubricants and mould release agents may lead to poor oxide formation.

3.3.1 The Basics Of Anodising

The naturally occurring oxide film on the surface of aluminium is an excellent form of protection against corrosion and surface wear. Anodising is an electrochemical technique used to grow that oxide film to a desired thickness. Thicker films provide greater protection to the substrate, whereas thinner films may provide visual benefits. The exact thickness of the oxide film can be controlled during the process of anodising. The thickness of the oxide film naturally formed on the surface of aluminium is around 0.013μm [13], but this can be increased to 250μm or greater for some anodising processes [84]. British standard 1615:1972 gives the minimum average thickness for an anodic oxide film for use as decorative car trim, as 10μm [84]. This standard has now been superseded by BS EN ISO 7599:2018

To achieve the growth of the oxide film, an aluminium part is submerged within an appropriate electrolyte and a current is passed through the part and solution. The aluminium part is made the anode and oxygen from negatively charged anions, present within the electrolyte, are deposited upon the surface. The reaction creates the strongly adherent film which is sparingly soluble in the electrolyte [84]. As the product is sparingly soluble, there is a balance between the rate of growth and dissolution of the oxide film. In addition, the rate of oxide film formation on the surface is dependent on the thickness of the film. As the oxide film increases in thickness, the electrical resistance it provides also increases, slowing the rate of oxide formation. Once this reaction of dissolution and deposition is balanced, the oxide film will stabilise at a given thickness. This depth of film is also dependent on the operating conditions, substrate and electrolyte present [84].

The structure of the anodised film could be expected to be a single thin

homogeneous layer on the metal surface; however, this is not the case. The oxide film consists of a thin barrier layer that forms next to the metal surface. The oxide film above this is porous and consists of interlocking hexagonal cells with cylindrical pores running through them all [85]. The dissolution of oxide film also opens pores within the oxide film that allow for dying of the film. Dye cations can be adsorbed within the pores, but subsequent sealing of these pores is then required to secure the cations and colour [86].

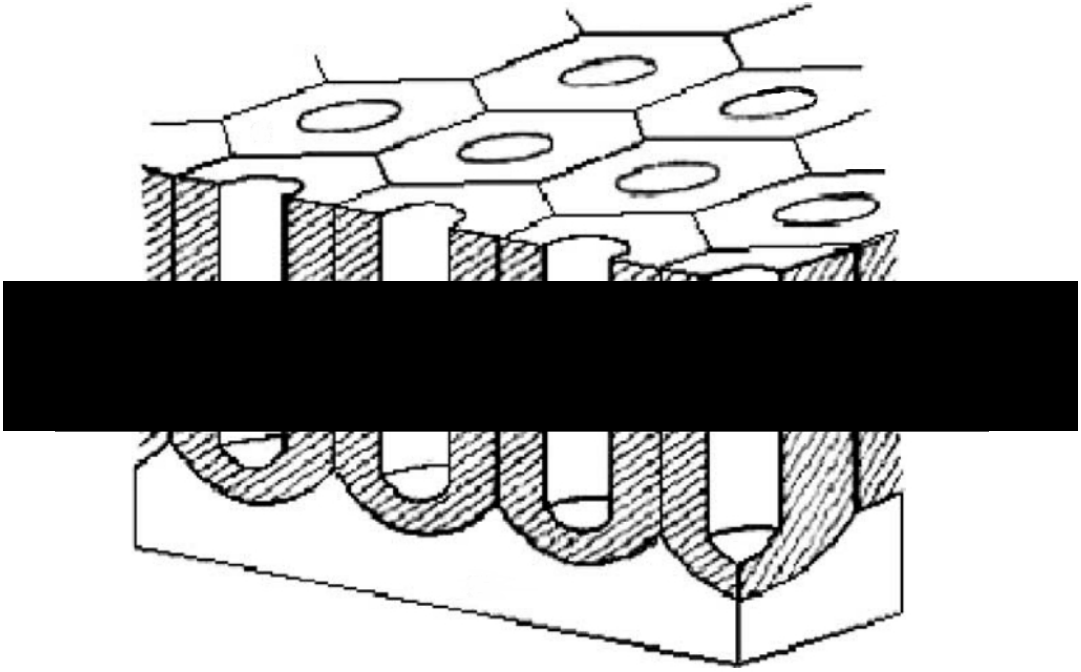

Figure 3.5: A diagram of the anodic layer formed on anodised aluminium [87]

3.3.2 The Types of Anodising

There are different reasons for anodising aluminium, including enhanced protection against corrosion and wear and for decorative finishes. Depending on the purpose of the anodising, the type of anodising will change. Different types of anodising mainly come from the variety of the different electrolytes that can be used.

Chromic acid is the original and oldest type of aluminium anodising. CrO_3 is the electrolyte which produces an opaque grey coating [13] on the surface of the substrate. Therefore, due to the colour and opacity of the coating, this process is mainly for the protection of the aluminium as oppose for a decorative application. The thickness of the oxide film ranges from around 2-15μm [84]. As visual appearance is a key element of brightware components, this technique is not appropriate for the application due to the colour and opacity of the coating formed.

Sulphuric acid anodising uses H_2SO_4 as an electrolyte to produce a clear oxide film that provides excellent corrosion resistance [13]. This thin clear film, 3-35μm in thickness [84], can be dyed to change the colour of the part. The clear film also means that a high gloss finish can be produced by first polishing the surface, and the protecting it with a clear anodic layer. These factors mean that sulphuric acid anodising is a good choice for decorative anodising and for protection of brightware parts.

Sulphuric acid is also used in hardcoat anodising. This anodising process produces a much thicker oxide film, about 50μm to 75μm thick [13]. The surface is formed is harder than tool steel and much thicker than other oxide films from sulphuric acid processes. Extra thickness can provide greater protection to the surface of the aluminium, at the cost of visual appearance.

Of these common processes for anodising aluminium, decorative sulphuric acid anodising is the one that is most applicable for possible use in automotive brightware and trim. Key to this, is the clear finish that this technique gives. The aesthetics of the brightware parts are paramount and other techniques, unfortunately cause a change of colour on the surface of the part. Hardcoat anodising would provide superior corrosion resistance to standard sulphuric acid anodising, but the thickness of the oxide film formed by the later process can be increased to improve corrosion resistance. British Standard B.S. 1615:(1972) details the required minimum average thickness necessary for anodic oxide films in different service conditions. The other benefit of the sulphuric acid anodising process is the design flexibility that could be provided when items of brightware can be anodised in a variety of different colours.

3.3.3 Aluminium-Silicon Corrosion Resistance

The initial review of aluminium alloys showed that the most common and castable were the Al-Si alloys. These alloys contain a large amount of silicon as the main alloying element within their microstructure. An alloy of A380 may contain up to 9.5wt% silicon and A383 used for greater detail and thinner walled castings could contain up to 11.5wt% [22].

L.E Fratila-Apachitei et al. [88] examined the formation of the oxide layer for hard anodising on Al-Si alloys containing up to 10wt% silicon. They found that silicon is anodised at a much slower rate than aluminium, which is a source of anodising problems for these alloys problems. The microstructure of Al-Si alloys is a mixture of aluminium dendrites separated by an Al-Si eutectic that contains intermetallic particles of silicon, as it is not possible for all the silicon to be dissolved within the matrix [89]. The difference in anodising rate leads to voids around silicon particles and porosity throughout the oxide film. Silicon was also found to block the electrolyte and increase the local resistance, which contributes to a less planar and uneven oxide barrier. As silicon particles remain in the oxide layer after the anodising procedure a barrier film is often formed encasing them [90]. The anodising process covers the silicon in an aluminium oxide film which is not strongly adhered to the silicon particle. This leaves a cavity which lowers the effective thickness of the oxide film. An example of this is shown in the image below.

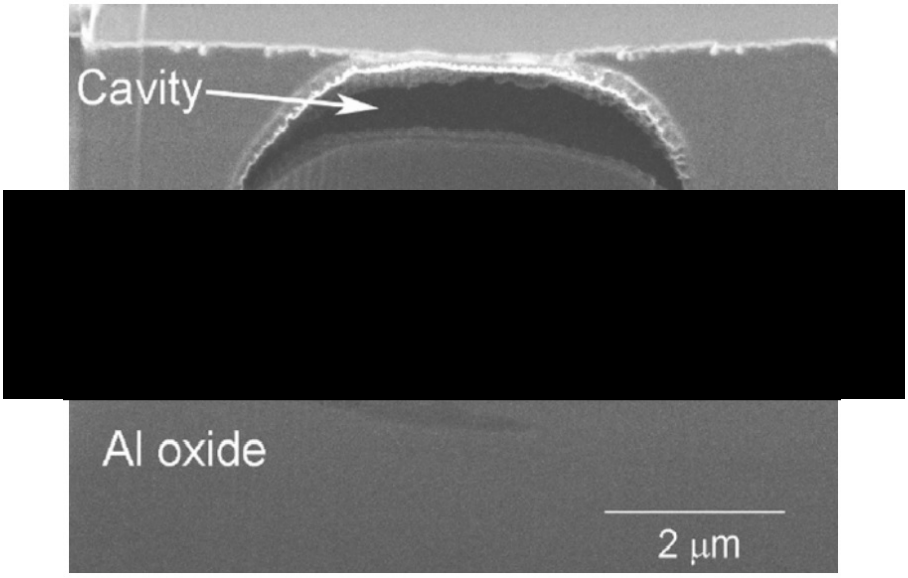

Figure 3.6: The cavity formed above a silicon particle during anodising [91]

This cavity is a weakness within the oxide film and therefore may become an initiation point for corrosion. Alternatively, the silicon particles strain the oxide film and become a source of cracks and defects. As the silicon content is increased the proportion of silicon eutectic in the microstructure will also increase. It seems intuitive that an increase in the microstructural constituent that disrupts the oxide film formation, will result in a poorer quality oxide. This is the case. B.Zhu et al studied the formation of oxide layer on cast aluminium alloys of different silicon content [90]. The silicon contents investigated ranged from 2.43wt% to 5.45wt%, which is significantly lower than for most of the common aluminium-silicon casting alloys. Some of the Al-Si casting alloys investigated have silicon contents of up to 13wt%. The thickness of oxide film formed by the anodising process was found to decrease with an increase of silicon content. So much so, that the thickness of the 5.45wt% alloy oxide film was approximately 70% of the thickness of 2.43wt% alloy [90]. The thickness of the oxide film in anodising can be controlled by processing parameters. In theory therefore, the issue of thickness is a solvable one, as changes to processing can be used to increase the thickness of the oxide film formed. However, as the silicon content is increases, the disruption to the oxide layer also increases. This may result in a thinner layer, as silicon particles lead to a uneven and poorly adhered oxide being created.

As processing changes can not avoid the damage to the oxide layer done by silicon, metallurgical changes have also been investigated. Silicon particles take the form of continuous flakes. However, particles can broken in to fibres with the addition of strontium as a modifier. While the silicon particles are in flake form, they can shield aluminium from anodising. This effect is reduced when they are separated in to fibres. In addition, the separated fibres induce less strain on the oxide after anodising and therefore, there is a large decrease in defects and crack in the oxide [89]. The overall effect is that there is a significant increase in the corrosion resistance for an anodised part. This modification is only mitigating the negative effects that silicon has on the oxide film and doesn't lead to a perfect, defect free oxide film being formed.

Despite the negative effects from the silicon, anodising of aluminium silicon parts is still completed. J.Konieczny et al [92] showed that anodising of an Al-Si-Cu cast alloy did increase the hardness of the surface, despite the poor quality anodic film that can be formed by anodising alloys with high silicon content. In fact, for the HPDC alloy tested, hardness increased 46% after anodising. This change shows that there are protective benefits to anodising Al-Si alloys, even though the oxide film is not optimised.

B. Zhu and C. Zanella investigated also investigated Al-Si samples that had been formed by rheocasting [93]. Hardness tested with a microhardness tester was completed on the anodised layer shows that resistance to deformation was increased dramatically with anodising. Hardness of the un-anodised sample was around 1.5GPa whereas an optimised anodising procedure increased hardness by almost three times to just over 4GPa. Interestingly, it was also found that hardness increased as distance from the surface increased. In the same investigation, the corrosion resistance of anodised Al-Si samples was also tested by immersion in salt solution was used to evaluate corrosion resistance. The path of corrosion for the anodised Al-Si samples was localised and originated from the area around the eutectic region. The open circuit potential of the as cast sample, with a 8.9μm oxide film, started at -0.685 V but decreased in the first 3 hours of exposure to salt solution to around -0.715V [93].

It has already been stated that large amounts of silicon can disrupt the formation of the oxide film. However, they can also change the colour of the film. This is not desirable for a brightware part for obvious reasons. Wernike [84] references Schenk when he describes the maximum amount of silicon that can be maintained within an alloy for a decorative casting as 2-3wt%. However, later, on Wernike states that 0.8wt% silicon can remain dispersed but excess silicon leads to a cloudiness when out of solution. At 5wt% the black and dark grey colours are achievable [84]. The vast majority of conventional Al-Si alloys contain far more silicon than 5wt%, let alone 2-3wt%. This means that for all standard alloys, anodising would lead to a cloudy/smutty finish which is not acceptable for decorative brightware. Without the protection of an anodised finish, the brightware parts would also be unlikely to withstand the required corrosion and performance testing necessary.

It may be possible (though unlikely) that using standard Al-Si alloys that haven't been anodised, could provide adequate corrosion protection. This is unlikely but it can be investigated. S.Cecchel et al evaluated the effect of salt spray corrosion on HPDC aluminium alloys for automotive components [94]. Three Al-Si HPDC alloys were tested. Two of these contained trace amounts of copper and the final alloy, EN AC-46000, contained 2-4wt% copper. Weight loss was slightly higher than 0.001g/cm^2 after 400 hours for the two standard Al-Si alloys. For the Al-Si-Cu alloy, weight loss was shown to be about eight times this value. Visual inspection of the samples after salt spray testing showed that the EN AC-46000 was obviously corroded. However, EN AC-43500 also showed visible signs of corrosion, even after cleaning,

that would not be acceptable for a brightware part. In addition, before cleaning, the effect of salt spray on the Al-Si alloys was visible at 50h. Therefore non-anodised Al-Si parts will be highly unlikely to last long enough to work as brightware parts as 50h is nowhere near the lifecycle of a car.

3.3.4 Aluminium-Magnesium Corrosion Resistance

Z.Hu et al investigated the corrosion behaviour of an Al-Mg_5-Si_2 alloy with a very similar composition to the Al-Mg5 alloy used for the experimental [95]. The drive to test the performance of these alloys came from the desire to use them for the HPDC of automotive components. Both permanent mould and HPDC samples underwent corrosion testing. The potentiodynamic polarisation measurement was completed using a platinum reference electrode and the weight loss from immersion testing was completed. The corrosion potential for this alloy was -1220mV, close to the Mg_2Si potential of -1150mV [95]. This lead to the conclusion that the $AlMg_2Si$ eutectic was crucial to the corrosion of these alloys.The weight loss of the samples was significantly lower for the HPDC samples as there were smaller grains and more grain boundaries. Mass loss was 220mg/cm^2 and 62mg/cm^2 for the die casted and HPDC samples respectively. Corrosion was focused along grain boundaries.

A similar mass lost test that Z.Hu used on Al-Mg-Si samples was employed upon Al-Mg samples by J.Yan et al [96]. They found that grain boundary dynamics played a massive part in the intergranular corrosion of these Al-Mg samples. These alloys were susceptible to sensitisation where Mg diffuses to grain boundaries and forms precipitates of Al_3Mg_2, which corrode preferentially. It was found by Yan.J et al. that sensitised Al-Mg alloys had a mass loss value that made them vunerable to intergranular corrosion. Whereas, when alloys weren't sensitised the mass loss was almost one fifth of the sensitised sample.

M.Okayasu investigated the corrosion resistance of two different cast aluminium alloys [97]. The first being ADC6 (Al-Mg) and the other being ADC12(Al-Si-Cu). Weight loss tests in salt solution for 336h showed that corrosion was significantly lower in the Al-Mg sample. Average mass loss was around 80mg/cm^2 per year for the Al-Mg samples. In contrast, for gravity casted samples, the corrosion rate of Al-Si samples was 400mg/cm^2 year, about five times the value. Interestingly, the corrosion mechanism for these two alloys is different. Al-Mg corrodes with intergranular corrosion whereas

Al-Si undergoes pitting corrosion. This experimental evidence would suggest that the corrosion protection of Al-Mg is superior to Al-Si alloys.

3.3.5 Aluminium-Zinc Corrosion Resistance

The final aluminium alloy system that requires review are the Aluminium-Zinc alloys. The corrosion behaviour of a cast Al-Zn-Mg alloy was investigated by A.V Sameljiuk et al. [98]. They found that the electrochemical potential of this alloys was around -700-715 mV with a passivation region of around 1600mV when tested with a silver/silver chloride reference electrode. This value is higher than was shown for an Al-Mg, earlier in this review. The role of intermetallics was also key for corrosion of the structure. Pitting corrosion was localised at intermetallics and smaller precipitates in the samples lead to a better corrosion resistance.

In terms of anodising Al-Zn alloys for increased corrosion resistance, this is more common with wrought alloys than cast ones. K Dejun and W. Jinchun both studied the corrosion performance of anodised 7475 wrought aluminium alloy [99]. Visual inspection using scanning electron microscopy displayed that anodising had limited the extent of damage caused by corrosion. In addition to this, N. Du et al studied the corrosion performance of 7050 aluminium wrought aluminium alloy and investigated the potential change due to anodising [100]. The reference electrode used in testing was a saturated calomel electrode [100]. The untreated surface had a electronegativity potential of -767-685mV. However, anodising the sample had a major positive effect on the electronegativity of the sample. A 4 micron film changed the potential to -154 to -87mV. This serious difference shows the protective effect of an anodic film on this alloy.

Chapter 4

Experimental

So far in this review, cast aluminium alloys have been investigated in more detail than other alternatives and three possible alloy systems have been identified in more detail. Experimental testing of these alloys was necessary, to investigate their suitability for brightware further. Initially, it had been the plan to test cast components of representative alloys. Due to financial and time constraints, just the raw material was tested. This is also why the review in to fluidity of alloys was completed, to provide data on the castability of alloys that would have been gained with casting of simple shapes. The aim the experimental testing was to investigate the performance of replacement materials over three key areas important for brightware parts: visual appearance, mechanical performance and corrosion resistance. Each test was chosen to provide information in one of these key areas.

Visual appearance is crucial for what are, normally aesthetic parts. This includes the gloss and reflectivity of the part of the part, as well as how uniform the part looks over the whole area. In order to test this area gloss testing and surface roughness profiles were completed. In addition, scanning electron microscopy and optical microscopy were also completed to study any coatings or layers on the surface.

Corrosion resistance is a key concern as any part needs to maintain a look over the lifetime of a part. Any corrosion product formed on the surface would spoil the look of a part. Therefore, exceptional corrosion resistance is required in order to stop even minor formation of corrosion product on the surface. Visual examination of corrosion is key to these parts. Consequently, an adapted outdoor salt spray corrosion test was used to compare the per-

formance of different alloys over time. In addition, open cell potential tests were also completed to gain a more analytical understanding of corrosion of the parts.

The mechanical performance of brightware parts could be overlooked as these components are not structural. All parts must be able to withstand moderate mechanical forces from windspeed, or maybe someone leaning on a part. It is expected that all the aluminium and zinc alloys would reach this level of performance. However, a key area that does need further investigation is the scratch and marring resistance of parts. It would not be acceptable for parts to have a tarnished look after a few weeks of use. In additions scratches on the surface would negatively affect the corrosion resistance of a part, especially if a surface layer had been penetrated. Hardness testing was completed to record the resistance to deformation of each surface for all the alloys tested.

As any replacement material would have to be able to meet an acceptable standard across every testing area. New aluminium parts were tested against existing zinc parts to provide a benchmark of performance.

4.1 Sample Preparation

In order to evaluate the performance of these aluminium alloys for brightware parts, an alloy from each of the different groups was sourced to undergo testing. This included an Al-Si, Al-Mg and Al-Zn alloy. In addition to these, samples of the Al-Mg and Al-Zn alloys underwent a procedure in attempt to anodise them. Therefore, in total there were five aluminium samples tested. Aluminium was supplied in 5kg ingot form by and consisted of one ingot of LM24/A380 and an ingot each of Al-Mg5% and one ingot of Al-Zn5%. The exact compositions of the aluminium ingots and a typical zinc casting alloy, are displayed in the table 4.1.

Table 4.1: The composition of the three aluminium alloys tested in the experimental and Zamak 5, a typical zinc casting alloy [9]

Alloy	Element wt%												
	Cu	Mg	Si	Fe	Mn	Ni	Zn	Pb	Sn	Ti	Cr	Be	Al
LM24	2.0-4.0	0.05-0.55	8.0-11.0	1.3	0.55	0.55	3.0	0.35	0.25	0.25	0.15	-	Bal
Mg5	0.1	5.23	2.40	0.13	0.44	0.01	0.02	0.01	0.01	0.03	0.01	0.028	Bal
Zn5	0.18	0.55	0.25	0.62	0.16	0.01	5.31	0.01	0.01	0.13	0.20	-	Bal
Zamak 5	0.75-1.25	0.03-0.08	-	0.100	-	-	Bal	0.005	0.003	-	-	-	3.5-4.3

The Al-Si alloy sourced is a standard alloy for casting and therefore, widely cast in to parts. Due to the difficulty of ordering such a low volume of aluminium, and the added fact that aluminium magnesium/zinc casting alloys are far less popular than Al-Si alternative, it was not possible to source ingots in this material that are the exact composition of casting alloys in every situation. The ingots of Al-Mg and Al-Zn supplied contain similar amounts of zinc and magnesium of alloys to existing casting alloys such as LM5 and LM31 respectively. However, they don't contain all the alloy additions that these alloys should also contain. The Al-Mg5% sample also contains around 2-3% silicon which is not present in LM5. Silicon has also been show to interfere with the anodising of the cast aluminium samples, early in the review of corrosion of Al-Si cast alloys.

The 5kg ingots were machined by Swansea University engineering workshop department using a bandsaw to produce two different sizes for the range of testing applied to them. Square samples of $5cm^2$ were taken from the centre of the ingot. These samples were approximately 1cm in depth. Rectangular samples of $2cm^2$ by 1cm were also taken from the centre of the ingot. These smaller samples were also around 1cm in depth. The smaller samples were then mounted in resin microscopy holders. The two different sizes of sample were necessary as different experimental tests required differently sized samples. An image for reference of the two sizes of sample is displayed below.

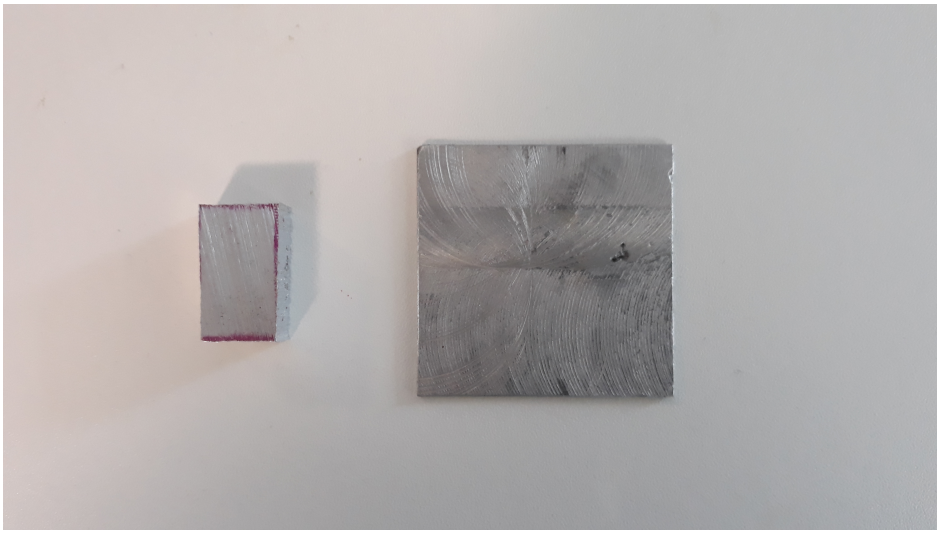

Figure 4.1: Examples of the two different sizes for tested parts

To benchmark the aluminium alloys against existing brightware parts, samples from two different types of brightware component were also tested. The first part chosen was a bezel for a rear seat belt. This bezel is cast in a hypo-eutectic Zn-Al casting alloy, and coated in a chrome electrocoat with a dark satin finish. This bezel was selected as it was quite a small and simple part. Therefore, it would be easier to cast than most other brightware parts. If castablility was an issue for aluminium samples then this would be the part that would have the best chance of being cast. Therefore, it is a good place to start to see if zinc could be substituted for aluminium. In addition, there were large parts of the surface of the bezel that were particularly flat, which is useful when creating samples for microscopy. The second brightware part was an exterior strake. Again, this was cast in the same zinc alloy but finished with a high gloss chrome electrocoat. The high gloss finish was important for a visual comparison and testing with aluminium samples to see if they could provide the same optical quality, especially after anodising. The other benefits of testing this second brightware part were that it is an exterior piece of brightware (unlike the bezel) and it had very large flat sections to allow for easier microscopic testing and imaging. Samples of the zinc were also machined in to the two aforementioned sample sizes using a bandsaw. The only difference being that the depth of the zinc samples was equivalent to their section thickness. This did not disrupt or change any of the experimental testing completed.

Figure 4.2: The two tested brightware parts. The low gloss part is on the top

All small samples of zinc and aluminium were mounted in epoxy resin using an ATM Opal 410 hot mounting press. The heating and cooling time were both four minutes and the maximum temperature was 180°C. Samples were prepared aligned both horizontally and vertically to allow for surface analysis and imaging of the cross section.

Samples were prepared for microscopy examination by hand, using the following grinding and polishing routine. Silicon carbide grinding papers were used during the grinding stage. The same grinding procedure was used for the preparation of zinc and aluminium samples.

Table 4.2: Grinding procedure used for the metal preparation of the aluminium alloys

Grit Size	RPM	Time	Lubricant
120	300	Until plane	Water
400	200	5 minutes	Water
600	200	5 minutes	Water
1200	200	10 minutes	Water

Mol Struers polishing cloths, made from wool, were used when polishing. A water-based lubricant was applied every 40 seconds. 6μm and 3μm water based monocrystalline diamond suspension was used as a polishing agent. Polishing was completed using each suspension for 10 minutes per sample or when all scratches were removed from the samples, whichever occurred first.

The larger aluminium samples, 5cm^2, also underwent the same grinding and polishing procedure. However, the polishing stage was only completed on the one large flat side of the sample that was to undergo testing. Due to the different sizes of the sides of each larger sample, the time taken for grinding and polishing of samples did not conform to the times in the table above. Personal judgement was used to decide whether a stage had been completed to an adequate standard. This sometimes led to steps being repeated to achieve an acceptable result.

4.2 Anodising Procedure

As previously mentioned, anodising of the Al-Mg and Al-Zn samples was attempted to improve the corrosion resistance of these alloys. Unfortunately, there was no specialised anodising equipment available to use within the

university. It was decided to attempt anodising within the university by re-purposing an electropolisher, rather than sending samples out to a professional anodiser for a small batch order. This course of action was chosen as it was much quicker to attempt the process in house. Especially, if there had been a failure or any complications in anodising samples professionally. This allowed time for the full range of testing to be completed on samples. In addition, although the job that would be done by a professional anodiser would be far superior, the optimisation of the anodising process for these aluminium samples is not the aim of the investigation. Anodising was completed more as an initial investigation, to see whether these samples could be anodised and what effect it had upon them. The cost of working on samples in house was also far lower.

Anodising of the aluminium samples was completed using an ATM, Kristall 680 electropolisher with the external external etching unit attached. Anodising was only completed on the larger 5cm^2 samples. The electrolyte was H_2SO_4 at 10% concentration by volume. The temperature of the electrolyte was monitored as the initial diluting of the acid caused an exothermic reaction. Testing only began when room temperature had been achieved. The supplied voltage was 15V. Unfortunately the electropolisher did not allow for the control of current , which would have been ideally kept at a level to maintain a current density of 1-2A/dm^2. The current density did go higher than this value. This method was taken from the surface treatment of aluminium vol 1 by S.Wernike and E.Pinnar [84] and aims to create a thin and colourless anodised layer. Once samples were submerged within the electrolyte the electropolisher was started and the samples, suspended by tongs, were gently agitated in the solution. Samples were immersed in the electrolyte for 5 minutes before being washed off and dried.

4.3 Accelerated Outdoor Exposure Test

The aim of the outdoor salt spray test was to evaluate all the samples against each other on their general corrosion resistance. It provided a visual reference for each part which in this situation, is very useful. A perfect result would be an aluminium sample showing no signs of corrosion, even when the current zinc samples did. This was very unlikely. However, the test also allowed the corrosion resistance of the aluminium samples to be ranked and see whether the anodising had had any noticeable effect.

The salt spray corrosion test used was adapted from the ISO standard 11474 for intermittent spray corrosion testing method. This was developed by Volvo for long judging corrosion performance over a long time period for automotive parts. The test does not aim to explain the mechanisms or reasons why a sample may corrode. It simply serves to show the performance of samples in a corrosive environment. This way, an easy to interpret visual comparison of the relative corrosion of samples can be observed. The test would normally be run over a much longer time but as the parts tested were not professionally finished, visible results occurred much sooner than usual.

The larger 5cm^2 aluminium samples were taped with PTFE tape around their edges and on the back to focus any corrosion over one single visual area. The whole range of aluminium samples, including the ones that underwent anodising were tested. As well as the aluminium parts, both of the current zinc brightware parts were tested. These samples were left outside at a 45°angle uncovered in Swansea for four weeks. Whole, uncut versions of each zinc part were secured at 45°outside. A salt solution of 5% concentration by volume was sprayed on all the samples twice a day, every day, for the full four weeks. The spraying of salt solution was scheduled twelve hours apart, once in the morning and once in the evening. This kept the addition of salt solution even across the day and test. Images of the samples were taken at 24 hours, 48 hours, 2 weeks, 3 weeks and 4 weeks. Any dried salt was rinsed from the samples before images were taken.

4.4 Open Circuit Potential

Analytical corrosion techniques can provide a more quantitative approach to studying corrosion. The open circuit potential of Al-Zn and Al-Mg samples, before and after anodising, was measured using a potentiostat. Large 5cm^2 samples were taped up with PTFE tape and a 3cm^2 area was left exposed for testing. The samples were then immersed in 5wt% salt solution and connected with crocodile clips to a Solartron 1286 Electrochemical Interference machine. A platinum reference electrode was also connected and immersed in the solution close to the exposed and corroding area. The open circuit potential is a measure of the thermodynamic driving force and tendency for corrosion to occur, a more negative number equates to a large driving force for corrosion. A coating or barrier may act to make this potential less negative [101].This indicates that the new surface of the material is thermodynamically more stable, which could lead to a reduction in corrosion rate.

However, this does not account for the kinetics of the corrosion reaction. Upon submerging the exposed part of the sample in salt solution, recordings were taken every second. Measurement of the OCP continued for a maximum of one day, although some tests were run for less time. The aim of the testing was to see how the open cell potential of the samples changed as the corrosion of the sample progressed and whether there was any change in potential after anodising the samples.

4.5 White Light Interferometry

Surface roughness is a key factor in the visual appearance for a part. A rougher surface will scatter more light, which will reduce the reflectivity of the part. Therefore, for a polished brightware surface should be as smooth a finish as possible is desirable. The surface roughness of a zinc part as well as the aluminium samples was examined using a white light interferometer. The other reason for completing surface roughness investigations on samples was to examine the difference in the surface profile before and after the attempted anodising process. If an oxide had been grown on the surface it might be expected to chane the surface profile of the part. A Wyko NT 9300 white light interferometer was used to measure the surface roughness of samples on a microscopic scale and generate 3D surface roughness maps.

4.6 Gloss Testing

Gloss testing is a standard test completed by Aston Martin Lagonda on brightware parts. Gloss is a measure of how well a surface reflects light, which is crucial for the visual appearance of a brightware part. If an aluminium part can be finished to a comparable glossy finish of existing parts, then it is fulfilling a significant visual requirement.

Testing was completed using a Rhopoint Instruments, Novo Gloss Trigloss Gloss Meter 20/60/85°. The three different angles for gloss measurement are related to the relative gloss of the sample. The three different angles available for the sample allow appropriate testing for different gloss values. Samples with higher gloss values should be measured at higher angles. As all the aluminium samples are aiming for a polished high gloss finish. The values of

80°were selected. This is most appropriate for measuring high gloss surfaces. Measurements were taken from a minimum of 5 different locations on any given sample to give an average GU value for the whole sample.

4.7 Microscopy

Both optical and scanning electron microscopy were used in investigating the surface layer present on samples. For aluminium samples this was the possible anodised layer and for the zinc samples, this was the chrome coating layer. Optical microscopy allowed for the chrome coating layer on the zinc to be studied and the scanning electron microscopy was used for studying of the thinner, and less easily detectable, anodised layer on the aluminium samples. For optical microscopy a Zeiss Primotech was used and for SEM investigation, a Zeiss Evo LS 25 was used.

4.8 Hardness Testing

The mechanical properties of the brightware parts are not overly taxing. Despite this, a key concern for brightware is the scratch and mar resistance. This is important for protection against long-term, damaging and aesthetically unpleasing scratches. Hardness is a measure of the resistance to plastic deformation for the surface of the material. Therefore, it allows a comparison of the alloys on a factor closely related to their scratch resistance.

An Innovatest Vickers Hardness tester was used to measure hardness for all the samples. The dwell time was kept constant at 10 seconds for all the tests completed. Two different forces were used in testing. These were 1kgF and 200gF. This was done to investigate the affect that a surface layer may have upon the sample. The thinking was that a thin surface layer would be easily penetrated by the 1kgF and not play any major role in the value of hardness measured. Whereas the 200gF may characterise the surface layer more effectively. Examples of all the different cast aluminium and zinc samples were tested in this way and each sample was tested a minimum of 16 times for each test. Care was taken to avoid testing to close to a previous indent so the sample was moved a minimum of 1mm after each test.

Chapter 5

Results

5.1 Mechanical Performance

5.1.1 Hardness Values

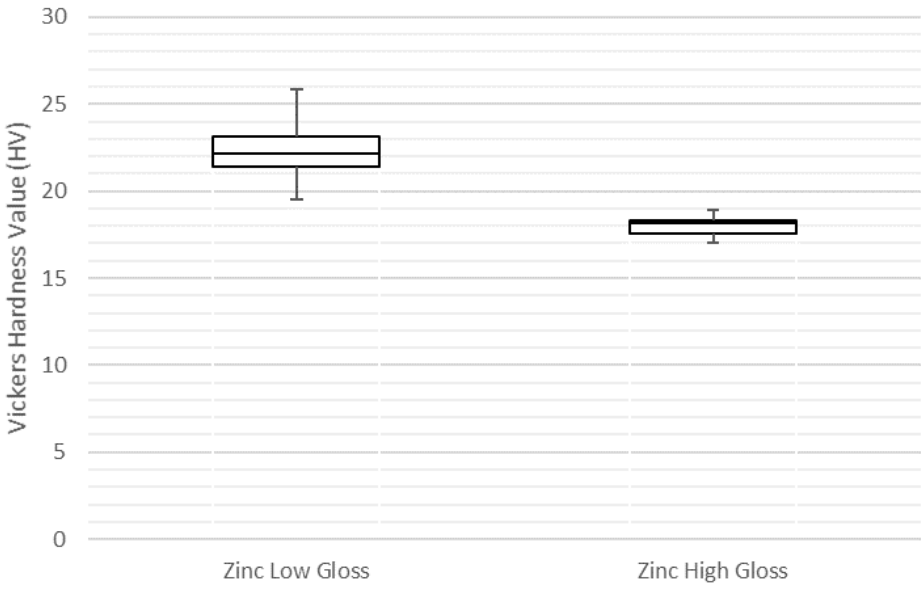

Figure 5.1: A comparison of the hardness for the existing low gloss and high gloss zinc parts, tested using 200gF. The zinc alloy used is a typical Zamak casting alloy, very similar in composition to the alloy in table 4.1.

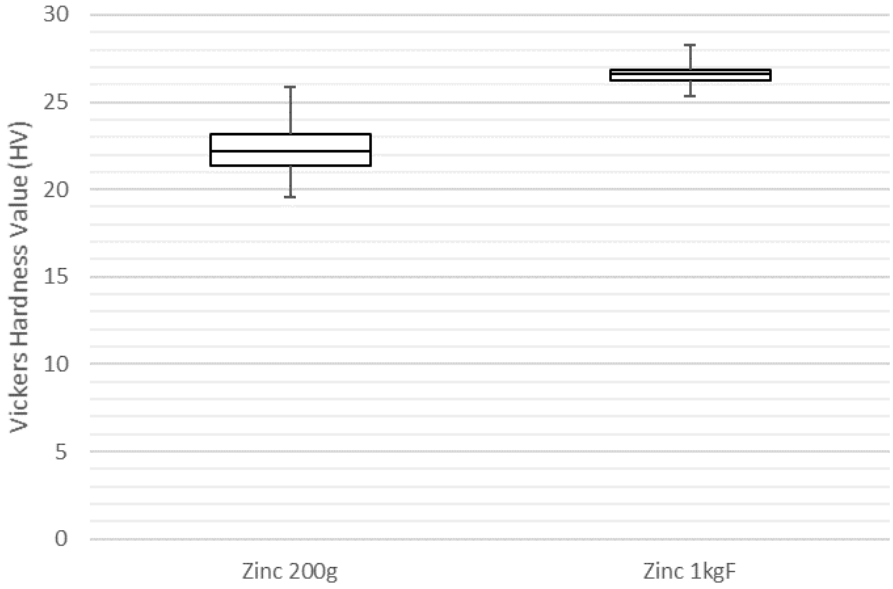

Figure 5.2: The effect of using different forces on the hardness testing of the low gloss zinc parts. The low gloss zinc alloy is very similar to the Zamak casting alloy in table 4.1

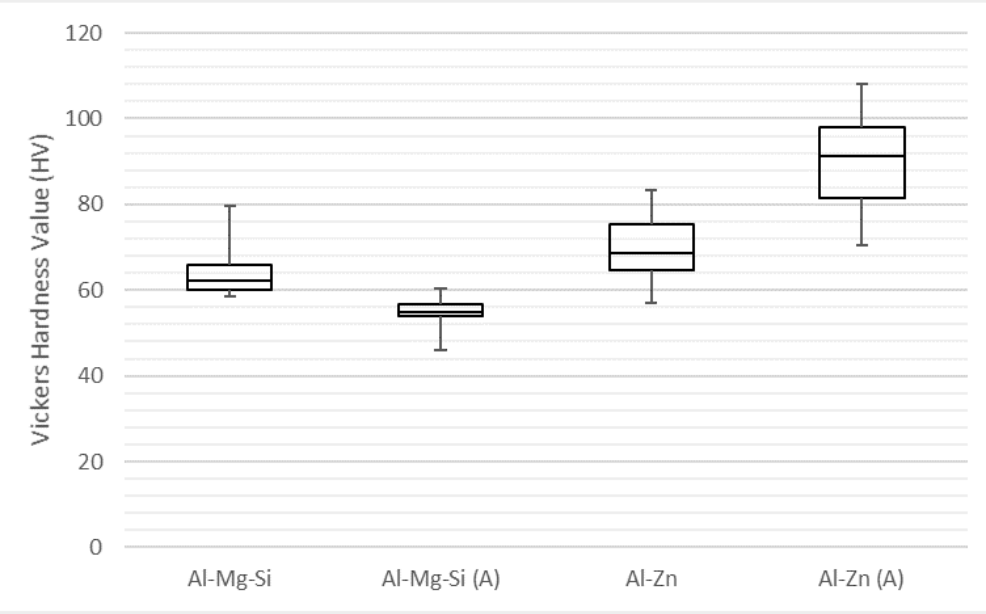

Figure 5.3: The difference in hardness of aluminium samples before and after anodising. The compositions of these alloys are visible in table 4.1 and they were tested at 200gF

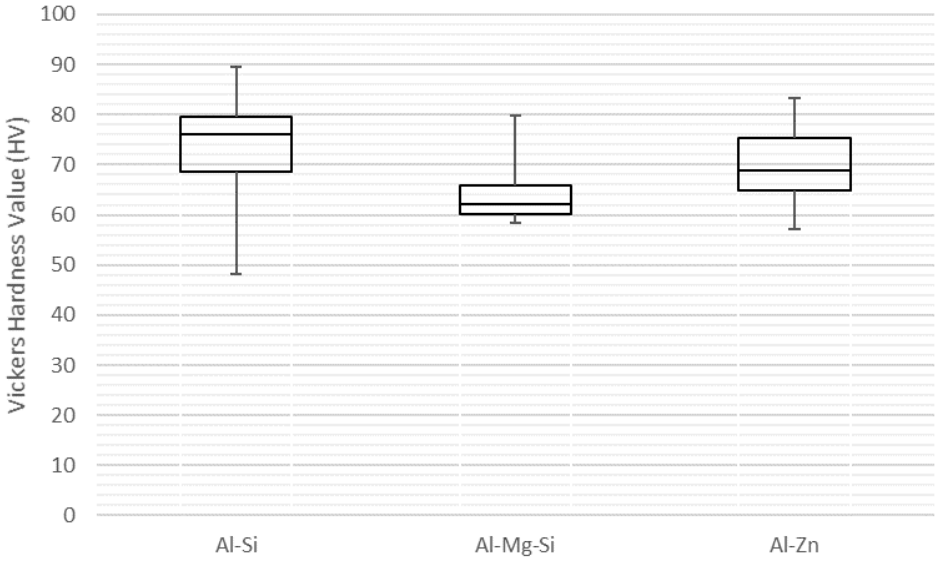

Figure 5.4: The hardness values of all the plain aluminium samples when tested at 200gF. The compositions of the alloys are visible in table 4.1.

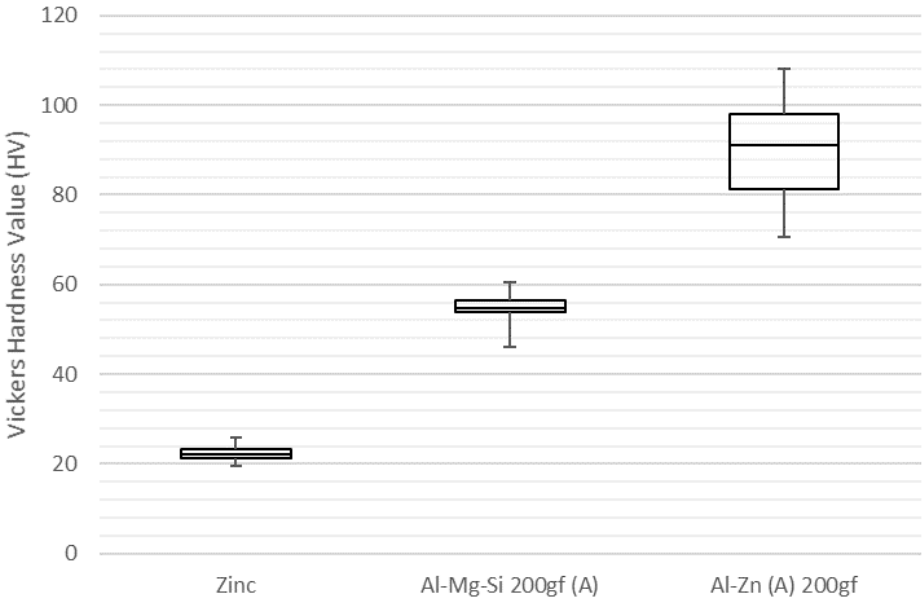

Figure 5.5: The hardness values of all the samples in a coated/anodised state to provide a comparison of parts performance in their finished state. The compositions are visible in table 4.1 and all samples were tested at 200gf. The zinc part is the low gloss finish variant.

Hardness measurements on the zinc parts for at different forces (fig 5.2) show that when 1kgF is used, the recorded hardness of the material is greater than for the 200gF. Initially, tests were only completed at 1kgF but as the value of hardness recorded was so low, a 200gF test was completed. The idea being, as the chrome layer was so thin, the indenter may be fully piercing it and measuring the hardness of other layers below. Therefore, by decreasing the force of the indenter, the chrome layer should play more of a role in the resulting hardness value. However, testing at this lower force showed that the hardness actually decreased. The conclusion drawn was that the low value of hardness wasn't from the fact that the soft layers underneath were being measured, but that the chrome layer wasn't actually that hard. There was concern that the mounting process for samples was causing heat damage to the chrome layer, so unmounted samples were also tested. These samples showed the same results as the mounted samples.

Both zinc samples show hardness values around 20Hv. The high gloss part was slightly less than this value, at around 18Hv. Whereas, the low gloss part is slightly greater at 22Hv. This could show that the low gloss

part has a slightly sounder and better formed layer than the high gloss part. All the aluminium alloys tested demonstrate a much higher hardness than the zinc brightware parts tested. The aluminium silicon alloy shows the greatest hardness performance of all the values, with the middle 50% of values recorded lying between 70-80Hv. This is massively more than for either zinc sample, in fact is about four times as much. The negative aspect to the aluminium samples, hardness is their range/spread in values with is much greater than the zinc samples. This is true of all the aluminium samples but particularly true of the aluminium-silicon alloy. That said, the lowest recorded values for the Al-Si alloy is around 50Hv, which is still over twice the recorded value for the zinc samples. The aluminium zinc and magnesium samples demonstrate similar Hv, with the median being around 70 for the Al-Zn and 62 for the Al-Mg. The range of values for these samples is also lower than for the Al-Si but still not as tight as for the zinc samples. Both samples show different behaviours after the attempted anodising procedures. The Al-Mg samples slightly decrease in hardness, but the difference is quite small. The Al-Zn samples show an increase from 70Hv to 90Hv after the anodising procedure.

Finally, comparing all the finished aluminium and zinc samples. There is a step increase in hardness performance from the zinc to the Al-Mg (a) to the Al-Zn (a) samples. The values of median are 22Hv, 55Hv and 90Hv respectively.

5.2 Visual Appearance

5.2.1 White Light Interferometry

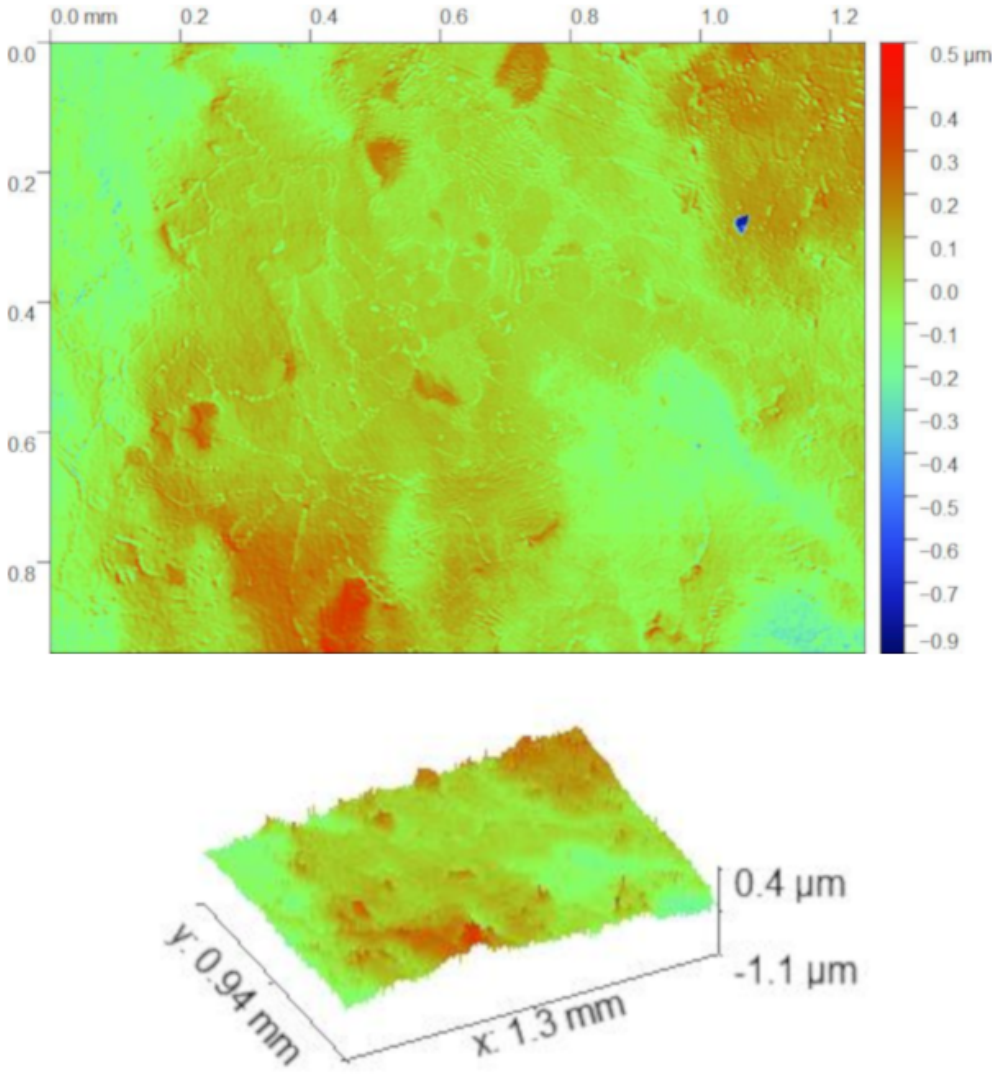

Figure 5.6: Surface mapping of a Al-Mg sample showing the roughness of the surface after polishing but with no other post processing

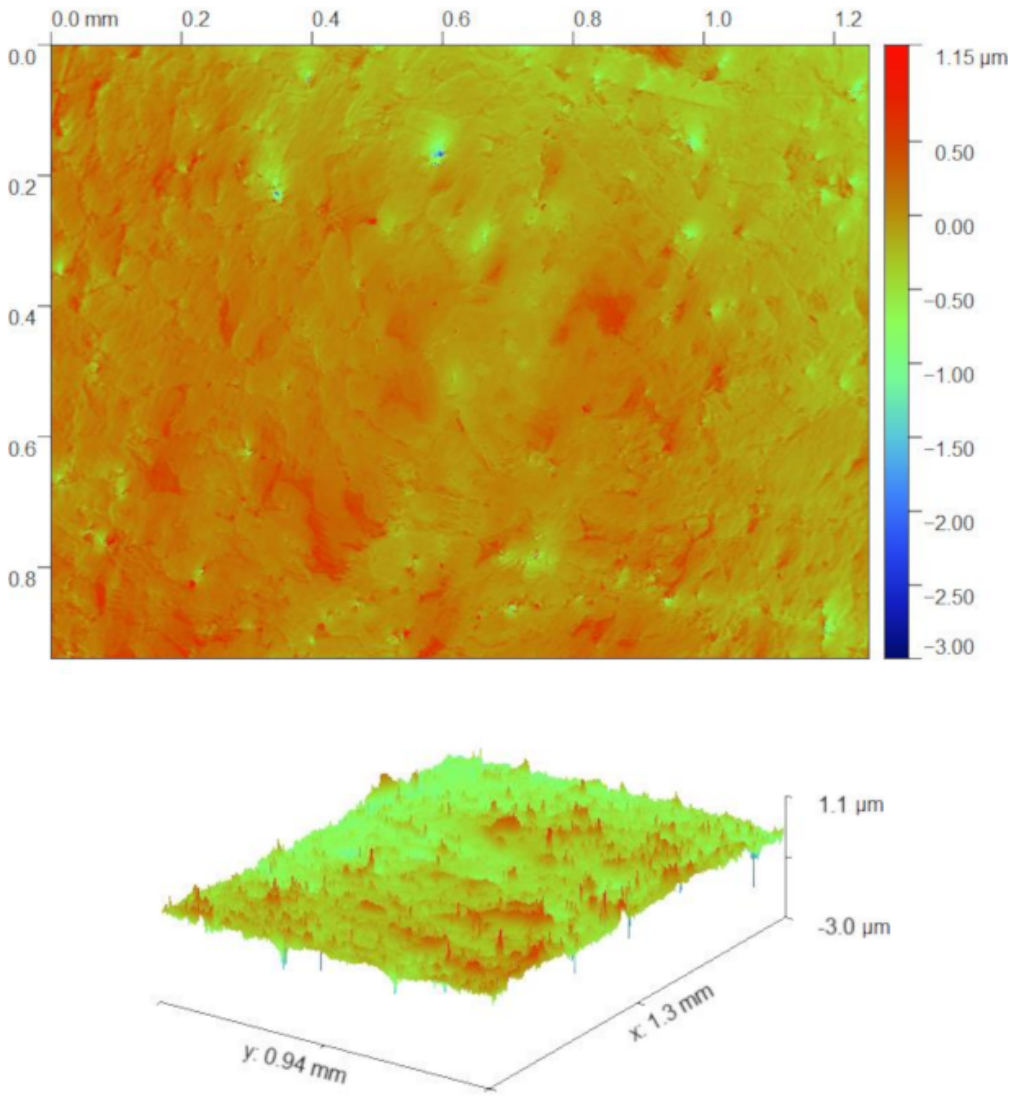

Figure 5.7: Surface mapping of a Al-Mg sample showing the surface roughness of the alloy post anodising.

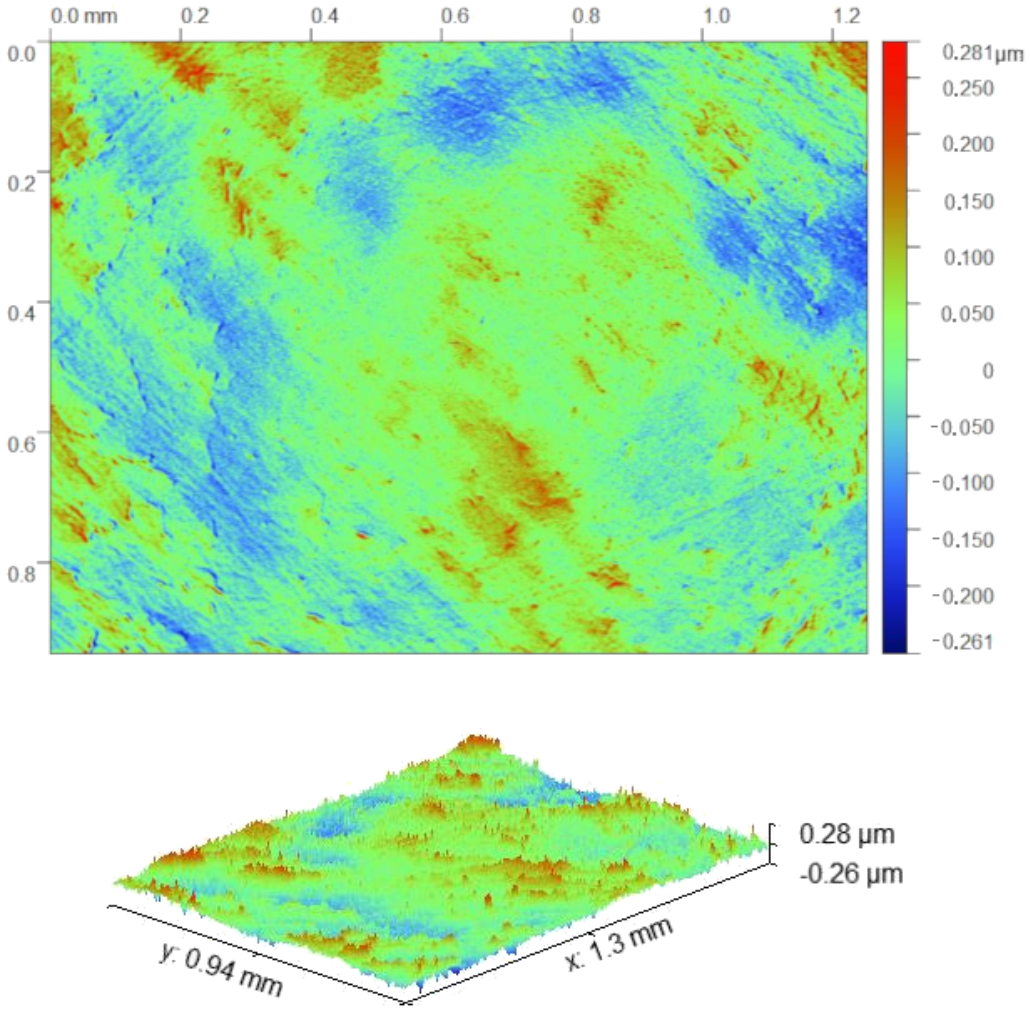

Figure 5.8: Surface mapping of a Al-Zn sample showing the roughness of the surface after polishing but with no other post processing

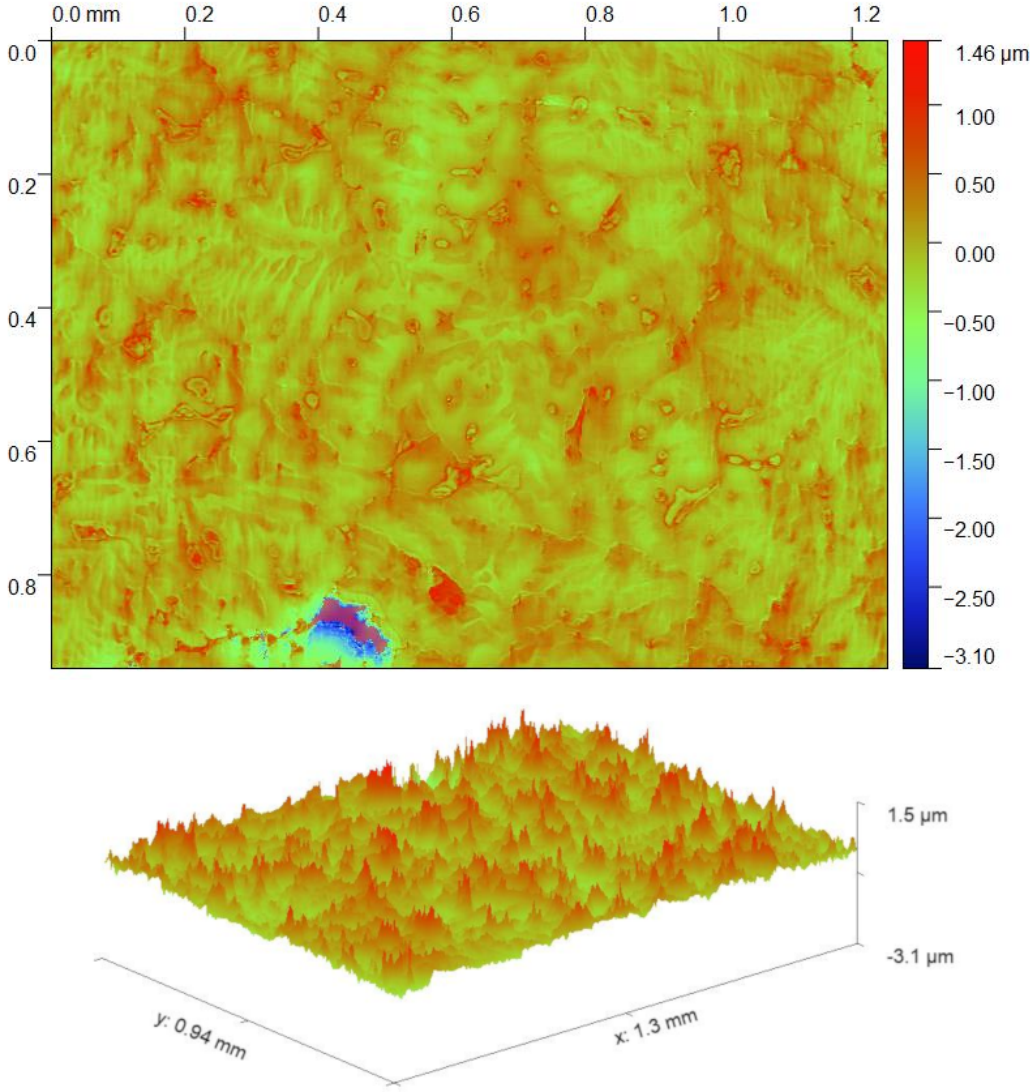

Figure 5.9: Surface mapping of a Al-Zn sample showing the surface roughness of the alloy post anodising.

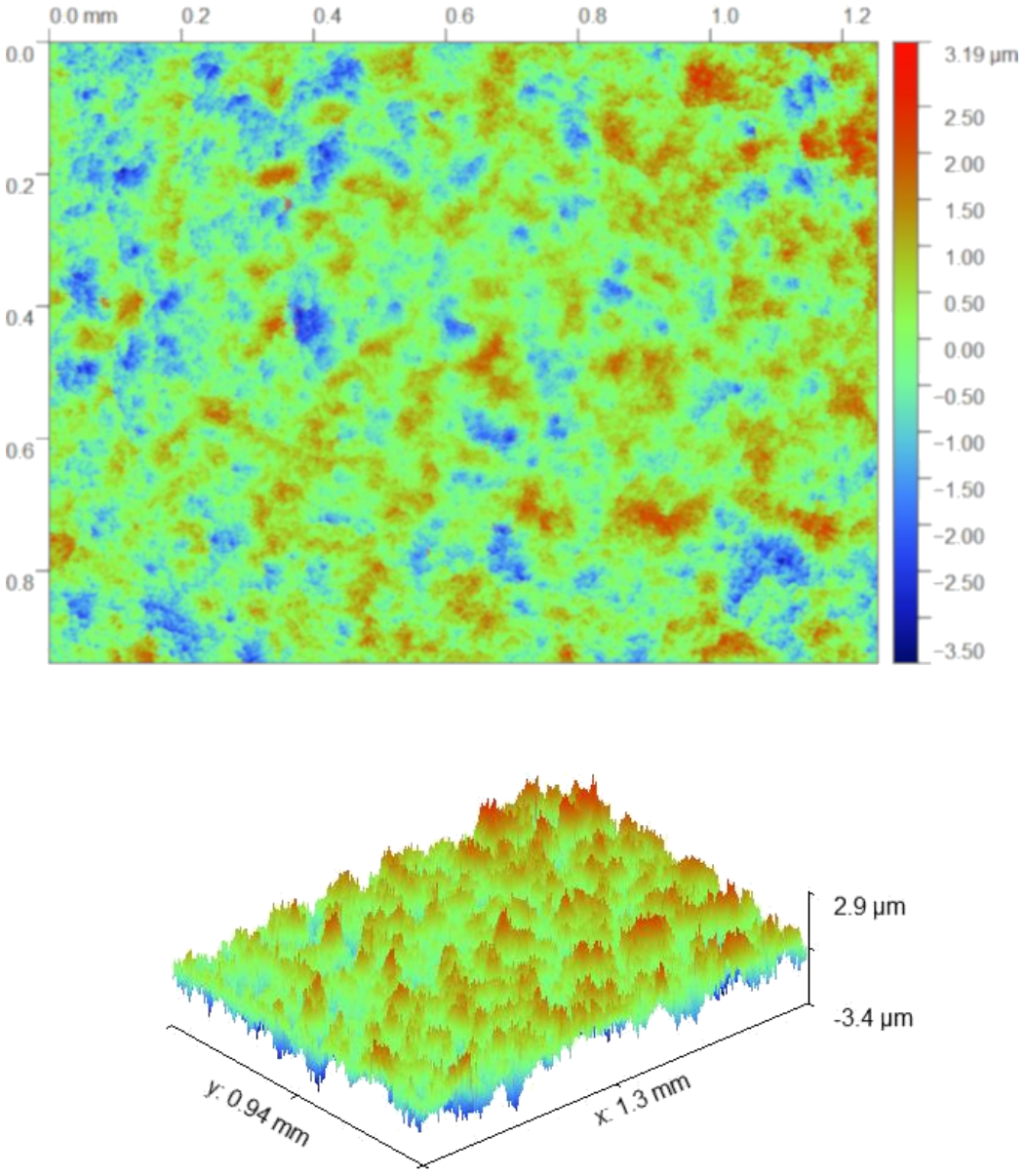

Figure 5.10: Surface Mapping of the High Gloss Zinc Sample displaying the surface roughness

The original polished surfaces of the Al-Zn and Al-Mg alloys show less topographical variation than the surface for the high gloss zinc sample. The 3D profile of the Al-Mg shows a flat surface with a few individual peaks reaching

0.4μm in height. The Al-Zn surface is similar with slightly more variations in height across the surface but a lower difference in maximum peak height of 0.28μm.

Post anodising treatment, the maximum peak size Al-Mg surface has tripled to 1.2μm but the amount of area on the sample that displays changing topography and roughness, has not increased much. There are more pits on the surface of the material. For the Al-Zn(a) samples, there is a large change in the in the overall surface roughness compared to the original sample. There are significantly more peaks and troughs present on the surface and the maximum height increases to 1.5μm.

Table 5.1: Statistical analysis of the surface roughness of the samples using the Gwyddion software. RMS stands for root mean squared.

Alloy	RMS Value for Surface Roughness (nm)	Average Roughness Sa (nm)
Al-Mg	95.07	72.49
Al-Mg(a)	156.9	116.6
Al-Zn	54.64	42.40
Al-Zn(a)	245.5	160.8
High Gloss Zinc Reference	712.1	562.3

The statistical analysis of surface roughness shows that there is an increase in surface roughness for both the of the plain aluminium alloys, after they have been anodised. This change is consistent for both the RMS and surface roughness (Sa) value. Both the anodised aluminium samples are still far less rough on the surface than the high gloss coated zinc part. Both the max height of 2.9μm and the overall number of peaks and troughs on the surface is greater for the zinc samples. The surface roughness value for the zinc reference of 562.3nm is around 3.5 times larger than the next highest value, belonging to the Al-Zn(a) sample.

5.2.2 Gloss Measurements

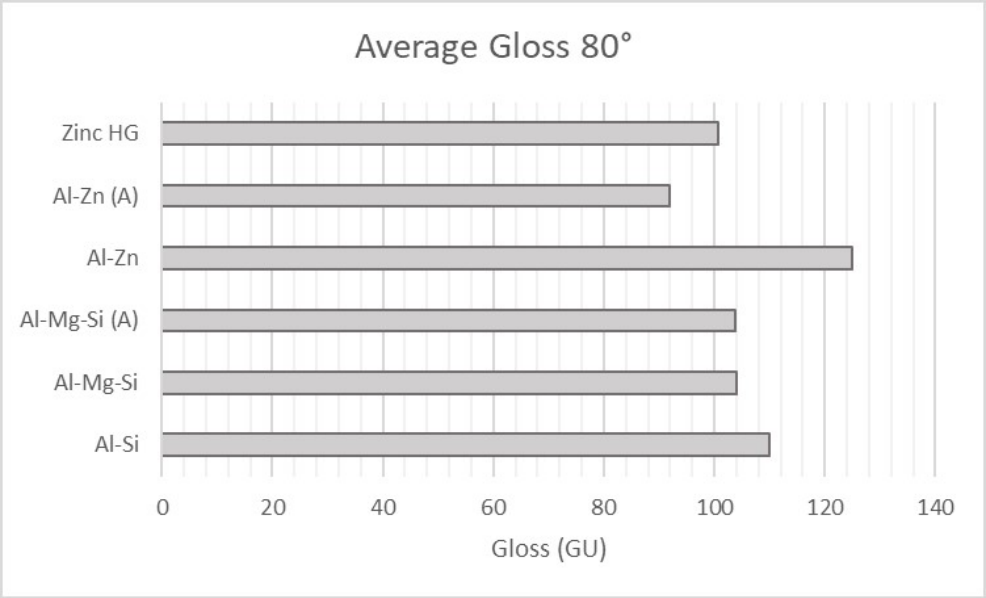

Figure 5.11: Average Gloss Measurements of all Samples

All the plain aluminium samples show gloss values greater than the zinc part reference. This is to be expected as these were not samples taken from a foundry but instead polished in a lab. The Al-Zn alloy does show a greater gloss value than the other samples which could show a greater tendency to be polished. Alternatively, it could also show that the porosity inherent in the Al-Mg sample has decreased the gloss measurement for this sample. After the anodising procedure, the Al-Zn alloy shows a marked decrease in the gloss level recorded. This is consistent with the visual change in appearance which saw the sample become slightly more cloudy on the surface. The Al-Mg sample shows no real change in gloss value. All the aluminium samples are within a similar point of the existing zinc parts for gloss value.

5.2.3 Microscopy

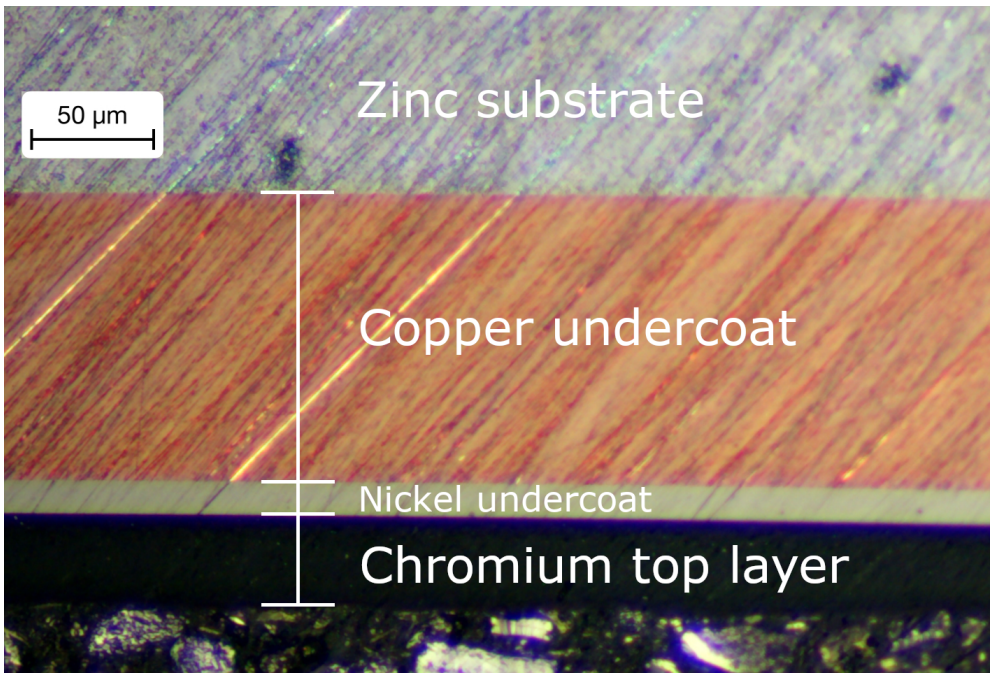

Figure 5.12: Cross Section of the coating on the low gloss current zinc part

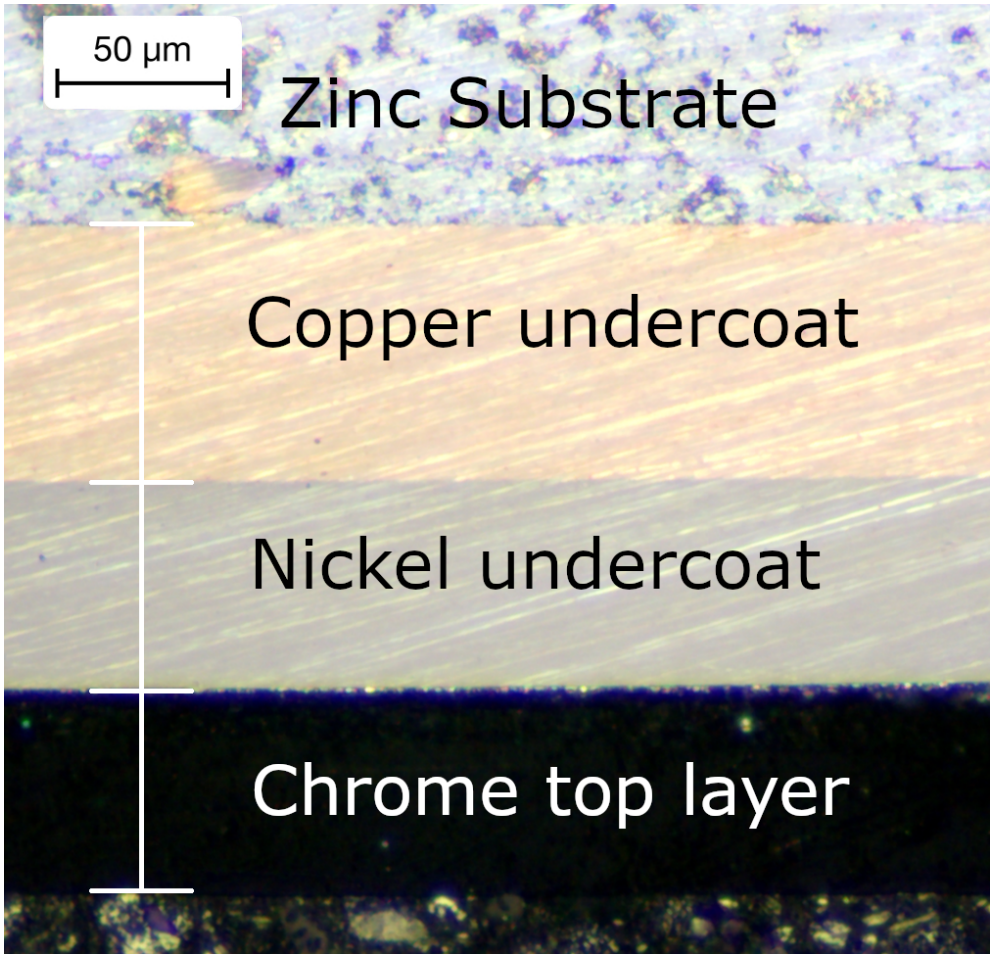

Figure 5.13: Cross Section of the Coating on the High Gloss Zinc Part

The size and proportions for the layers for the chrome coating are different between the two different zinc parts. For decorative chrome coatings, undercoats of copper and nickel are used [13]. By counting pixels in the layers and using the scale bar as a reference, the thickness of each layer can be calculated. These thicknesses are shown in the table below.

Table 5.2: The layer thicknesses of the electrocoat present on the zinc samples

Layer Measured	Zinc Low Gloss (μm)	Zinc High Gloss (μm)
Copper Layer	115.6	73.3
Nickel Layer	13.3	59.4
Top Layer	36.4	56.7
Total Thickness	165.3	189.4

The overall thickness of the high gloss part is greater than the low gloss part. In addition the thickness of the top layers and nickel layer are greater for the high gloss part, the copper layer is much larger for the low gloss alternative.

Scanning electron microscopy was necessary to examine the surface of aluminium samples as the oxide film formed on the surface is much thinner than the electrocoat layer on the zinc samples. Anodising is completed for Aston Martin on some wrought aluminium parts for different areas of their cars. A sample of one of these grill sections was obtained in order to study the size and quality of the anodic layer. This was a wrought alloy of unknown composition, the main focus is the quality of anodic layer that is already deemed satisfactory for Aston Martin parts. This should provide an excellent reference to the Al-Zn and Al-Mg anodised sections.

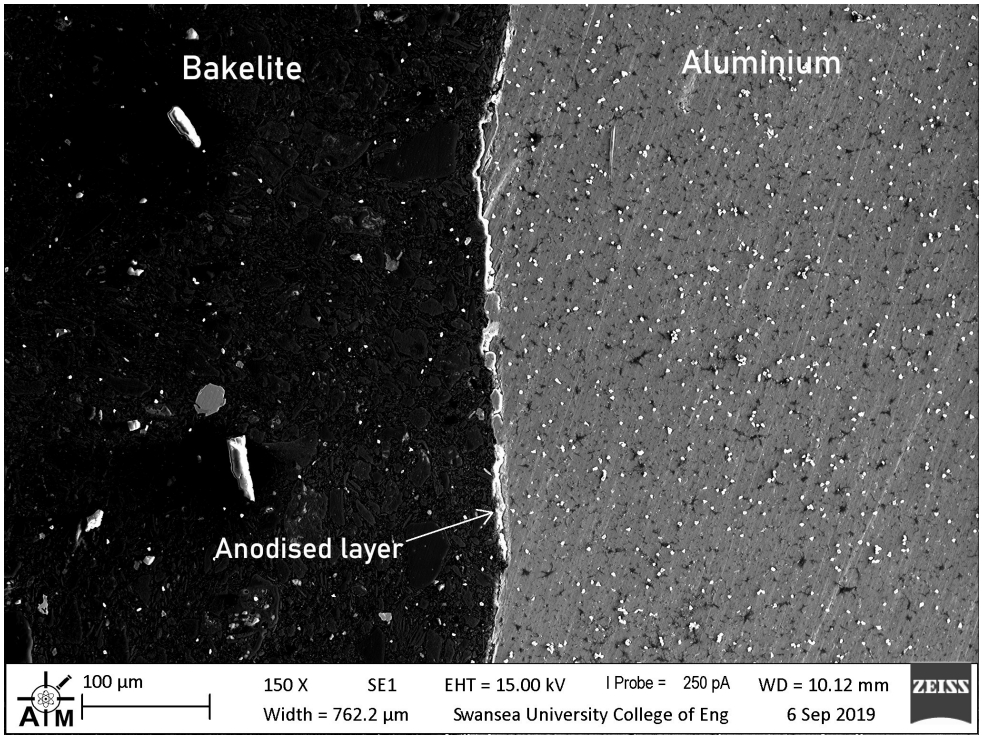

Figure 5.14: A high contrast image of the anodic layer on the wrought grill samples

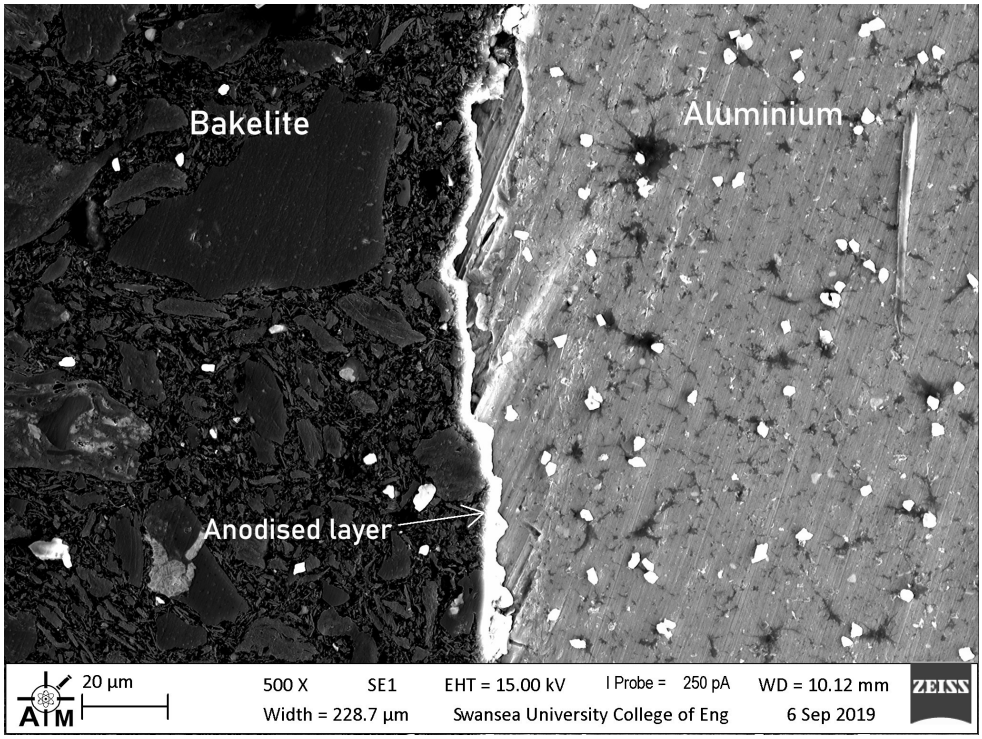

Figure 5.15: A high contrast image of the anodic layer on the wrought grill samples

The film formed on the wrought sample is approximately 7.5μm thick is the largest point. The oxide layer formed is consistent across the whole sample but the thickness does vary. These images of the anodic layer on the wrought sample were taken from the part of the sample with the best appearing surface film and some parts of the samples appeared to have much thinner oxide films than the one displayed in the images above, the anodic layer was consistent across the whole sample .

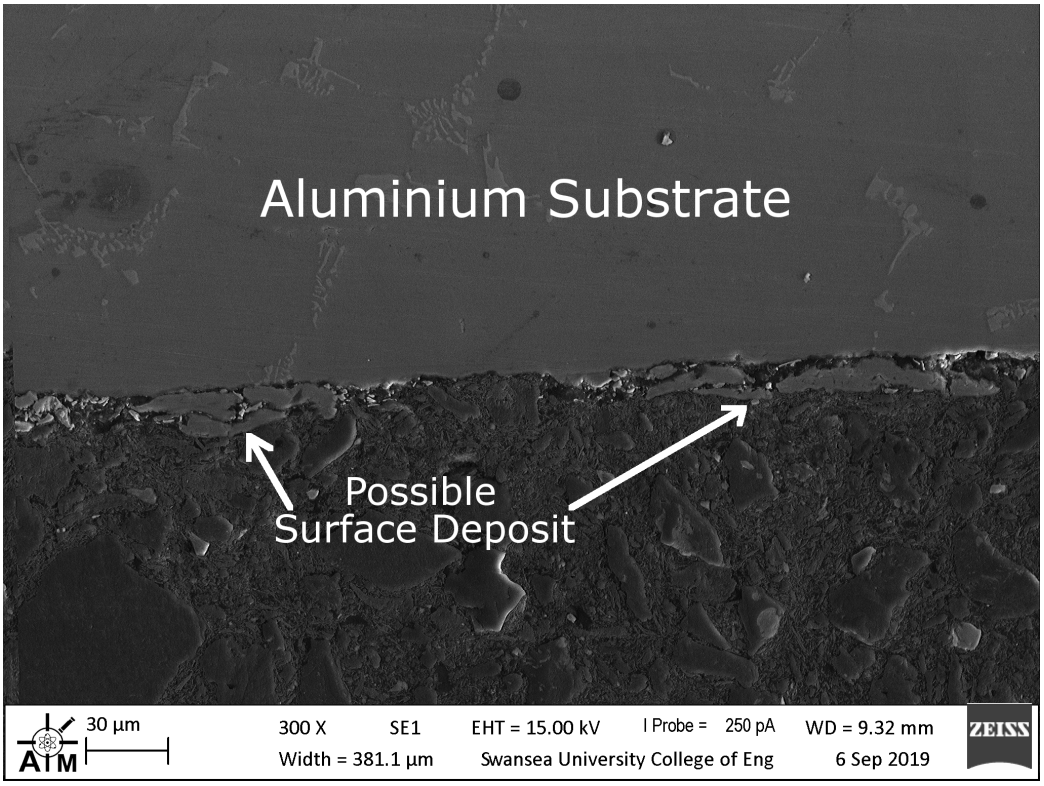

Figure 5.16: A section of deposit on the surface of the Al-Zn(a) sample

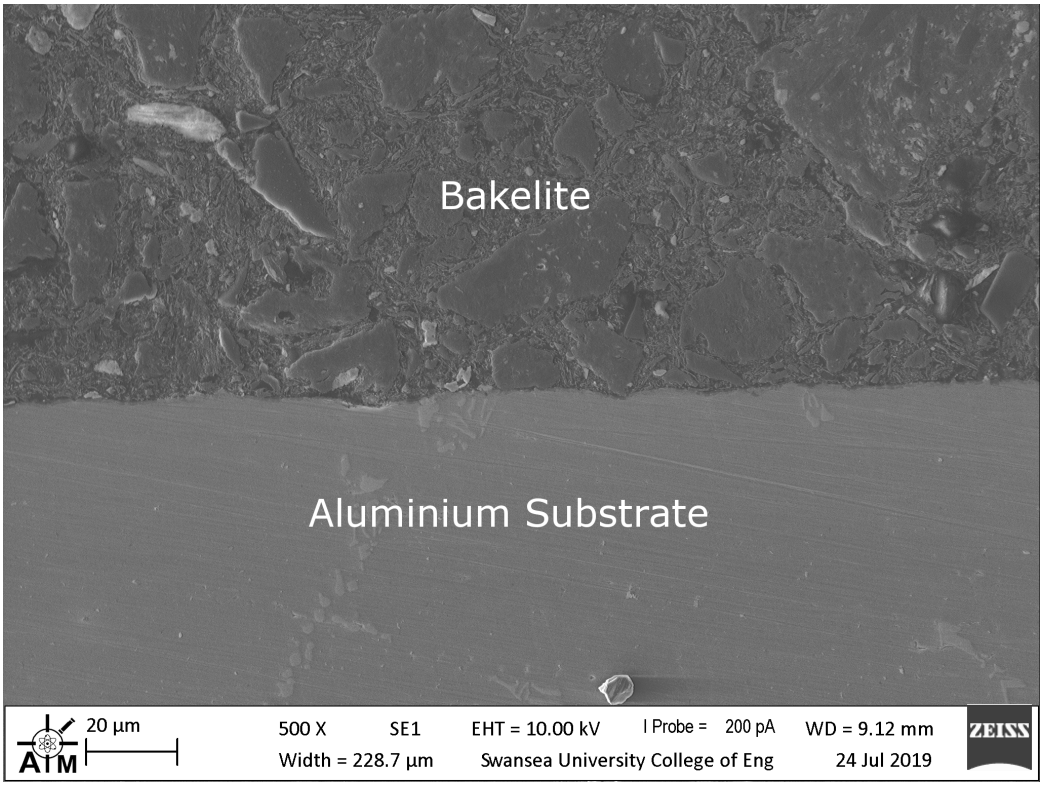

Figure 5.17: A section of Al-Zn(a) alloy with no visible deposit on the surface

Above is the cross section of the aluminium-zinc sample after anodising procedure. There does seem to be some deposit on the surface but it also appears very similar to the substrate material. If this is an anodic layer it is very poorly adhered and uneven across the sample. It is possible that this is also just material that has chipped off the surface of the material. It may also be that any anodic layer formed is so thin, it is very difficult to image. The natural oxide layer formed is only 0.013μm [13], which would not be possible to see on these images.

5.3 Corrosion Resistance

5.3.1 Accelerated Outdoor Exposure Test

Figure 5.18: Photos recorded of the Al-Si alloy. The sample is a 5x5cm^2 section of metal with PTFE tape surrounding the edges. It is the same alloy on each picture

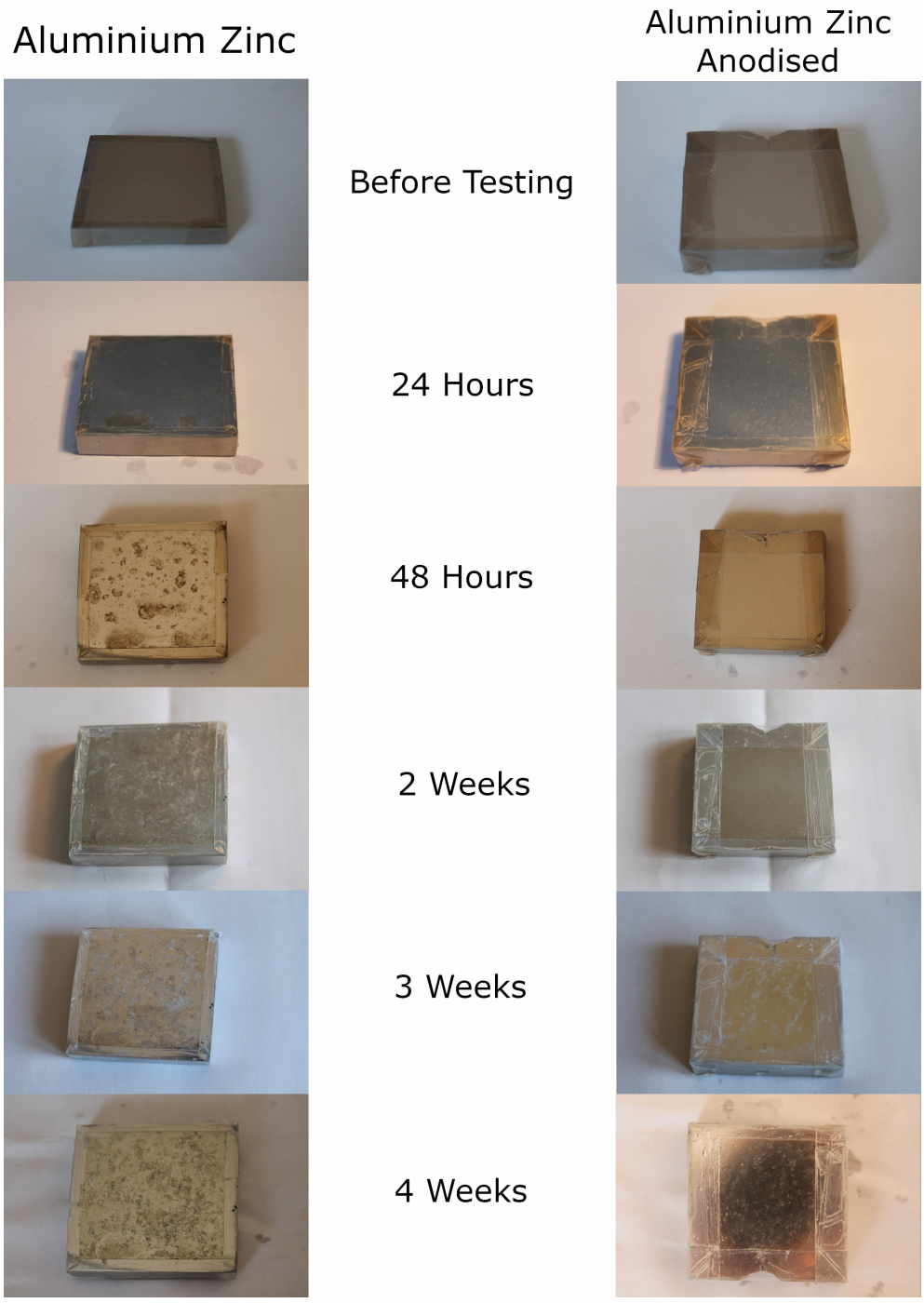

Figure 5.19: Photos of the Al-Zn alloy and the anodised partner. The samples are 5x5cm^2 sections of metal with PTFE tape surrounding the edges. The pictures show a the progress of corrosion on the surface for the same sample with an increasing exposure time.

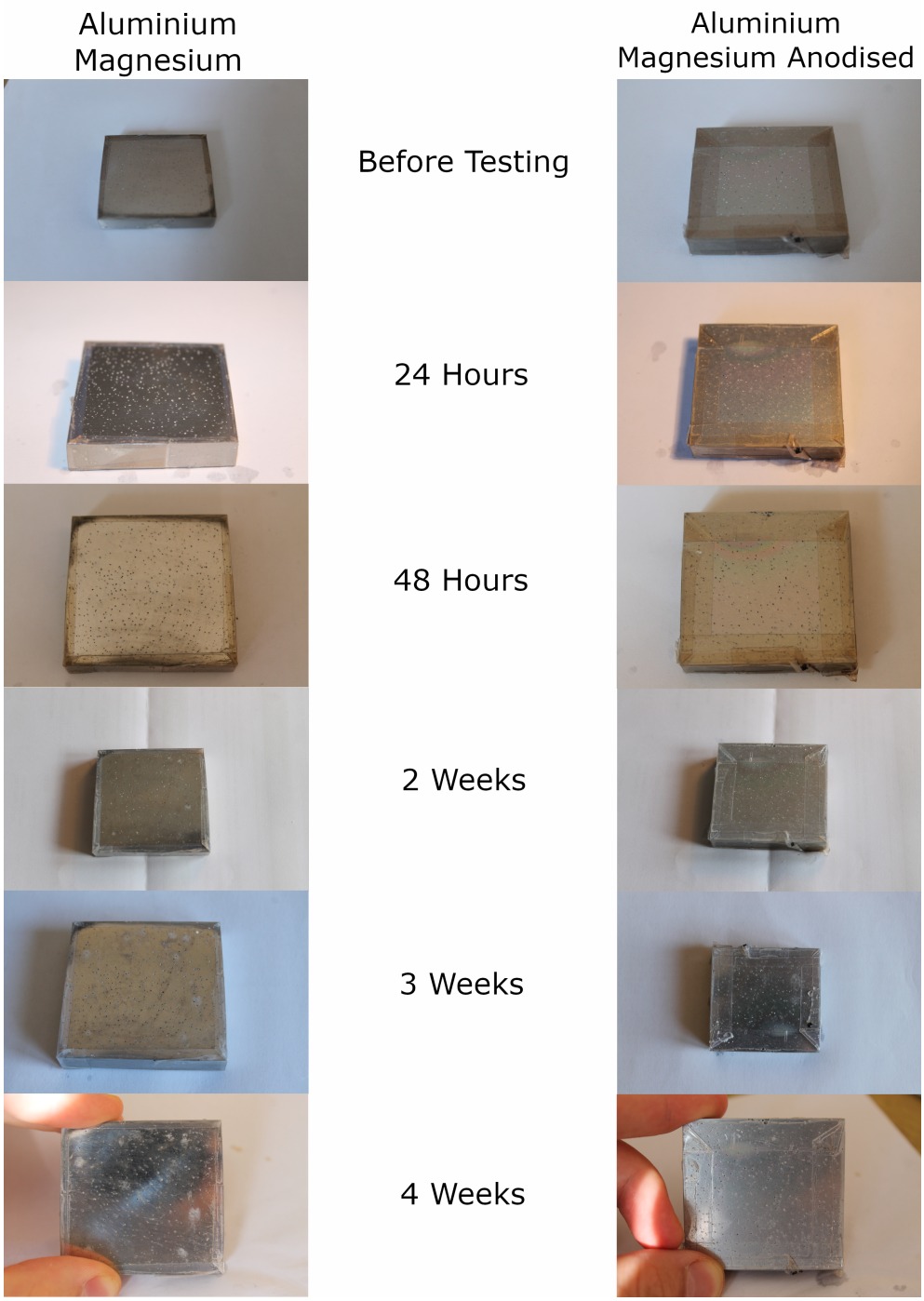

Figure 5.20: Photos of the Al-Mg-Si alloy and the anodised partner. The samples are 5x5cm^2 sections of metal with PTFE tape surrounding the edges. The pictures show a the progress of corrosion on the surface for the same sample with an increasing exposure time.

Figure 5.21: Photos of the two zinc parts before 4 weeks of exposure

Figure 5.22: Photos of the two zinc parts after 4 weeks of exposure

As seen from the imaging of the aluminium samples that had undergone the salt spray testing, all the aluminium samples showed some signs of corrosion on their surface after 4 weeks of exposure. The two images of the high gloss

and low gloss zinc parts show that these parts had not shown any signs of corrosion on their surface after 4 weeks. Therefore, all of the samples did not reach the benchmark, provided by the current zinc, chrome coated parts. Within the aluminium samples, there is a wide range of performances. The worst performing aluminium alloy, which shows the visual effects of corrosion earliest, is the Al-Si alloy. Even after only 24 hours, which is only two exposures to salt solution, there is extensive pitting across the surface as well patches of staining across the surface. The level of corrosion on the surface increases to 2 weeks where practically whole surface is transformed and severely corroded.

The next worst performing aluminium alloy is the standard Al-Zn sample. As with the Al-Si sample, there is corrosion product build up on the surface of the alloy after only 24 hours but not the same pitting corrosion present on the Al-Si sample. This corrosion product increases on the sample up to 2 weeks where the whole surface is mostly consumed, a similar time scale to the Al-Si alloy. The intensity of corrosion on the surface then increases to 4 weeks but unlike the Al-Si alloy, there are parts of the surface after 4 weeks that are not fully corroded.

The unaltered alloy with the greatest performance is the aluminium magnesium alloy. This alloy shows no visible signs of corrosion up until 2 weeks where around 4 or 5 small white spots are present on the surface. The size and number of these white corroded areas increases to the final image at 4 weeks. However, amount of corrosion product build up on the surface does not accelerate to the level of other samples plain aluminium samples tested.

Both the anodised samples demonstrate an increased corrosion performance to their un-anodised equivalent. For the Al-Mg sample, there is a patch on the sample from the anodising process that could be mistaken for corrosion but is present from the original image. The aluminium magnesium shows the first signs of corrosion as a white patch on the side after 3 weeks. This is at least a week later than signs appearing on the standard Al-Mg sample, 50% longer than the standard sample. This increase in performance is good but far less than the increase in performance from the Al-Zn sample. The anodised version of the Al-Zn has a small white patch of corrosion present at 2 weeks, whereas the plain sample shows more extensive corrosion, even after 24 hours. The corrosion of the Al-Zn anodised sample does spread more rapidly once corrosion has been initiated, than the Al-Mg samples. This possibly suggests that once any oxide layer failed it could not effectively re-heal.

5.3.2 Open Cell Potential

Graphs of the open circuit potential for the Al-Mg and Al-Zn, as well as anodised variants, are displayed below. The test was repeated for all the samples up to 4 times in order to try and establish a genuine trend. A low gloss zinc samples was also tested and displayed below.

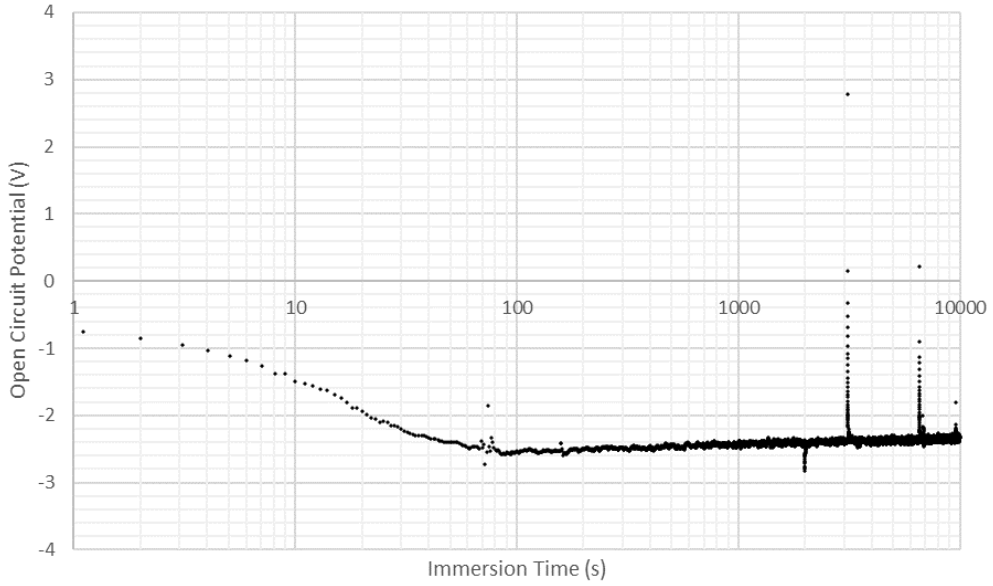

Figure 5.23: The graphed open cell potential for a low gloss zinc reference sample

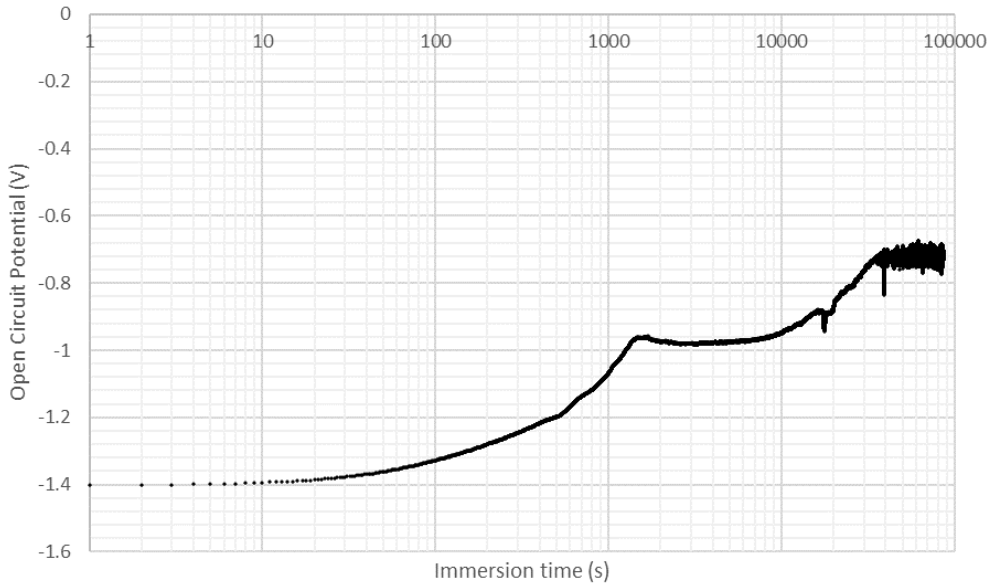

Figure 5.24: Graphed open cell potential of the Al-Mg alloy

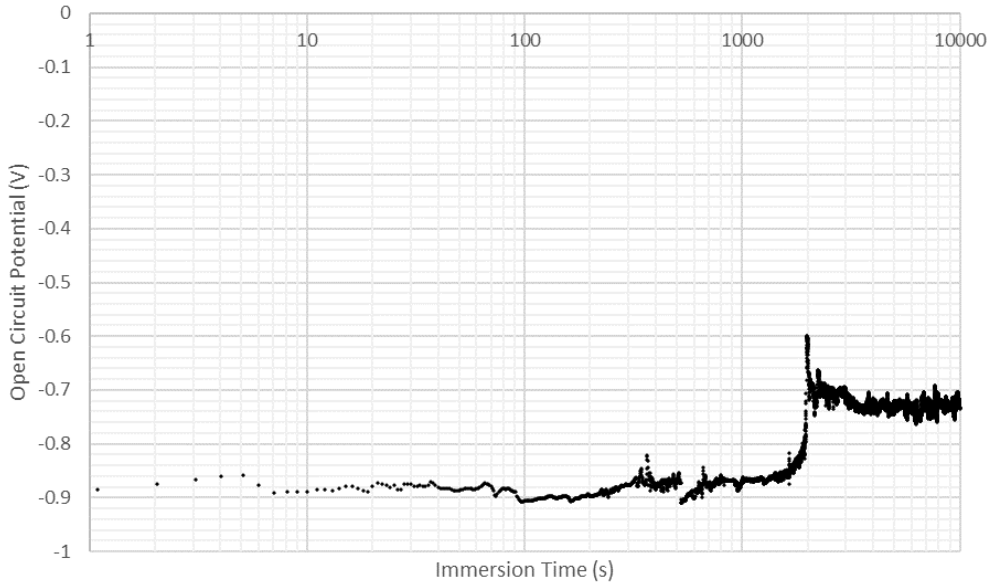

Figure 5.25: Graphed open cell potential of the Al-Mg(a) alloy

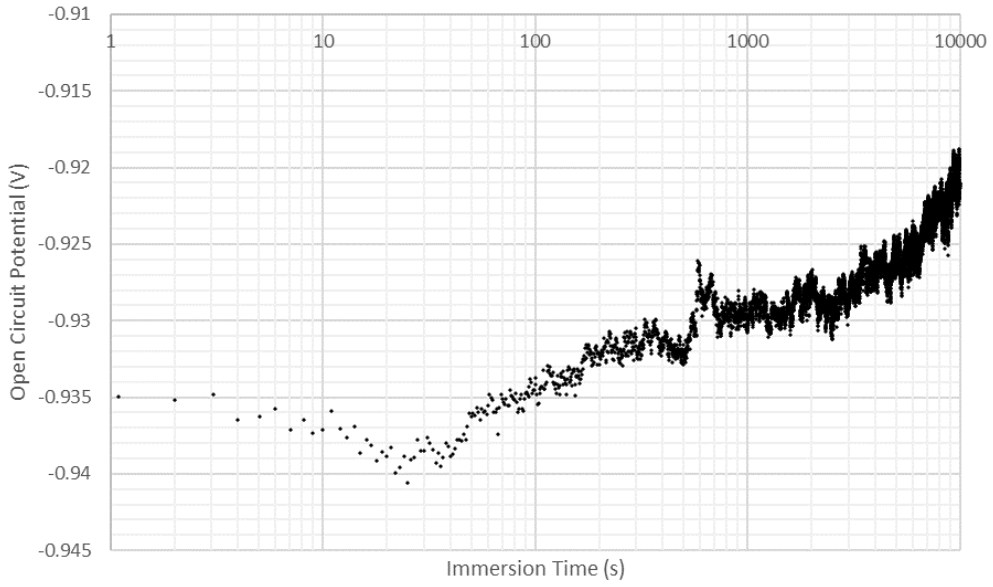

Figure 5.26: Graphed open cell potential of the Al-Zn alloy

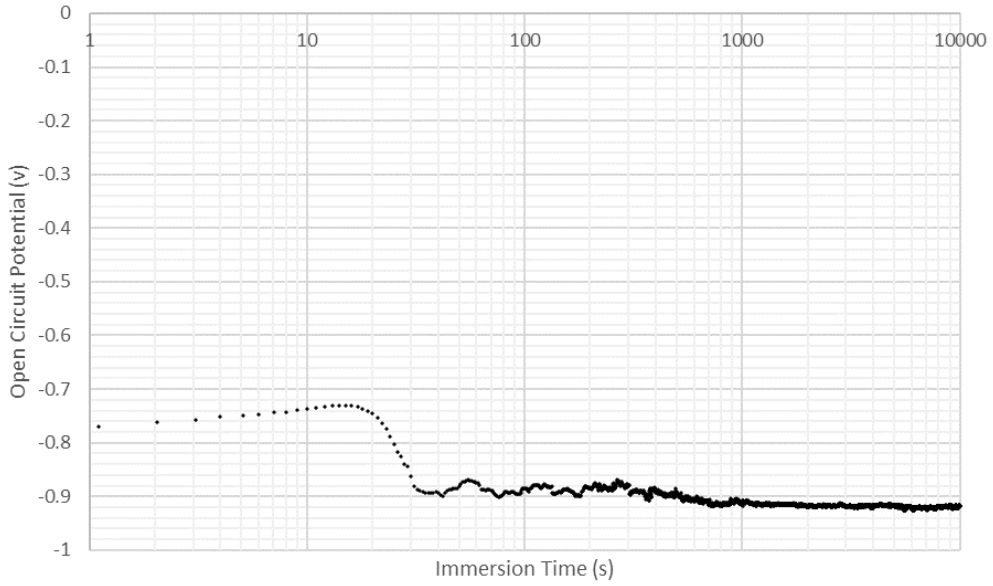

Figure 5.27: Graphed open cell potential of the Al-Zn (a) alloy

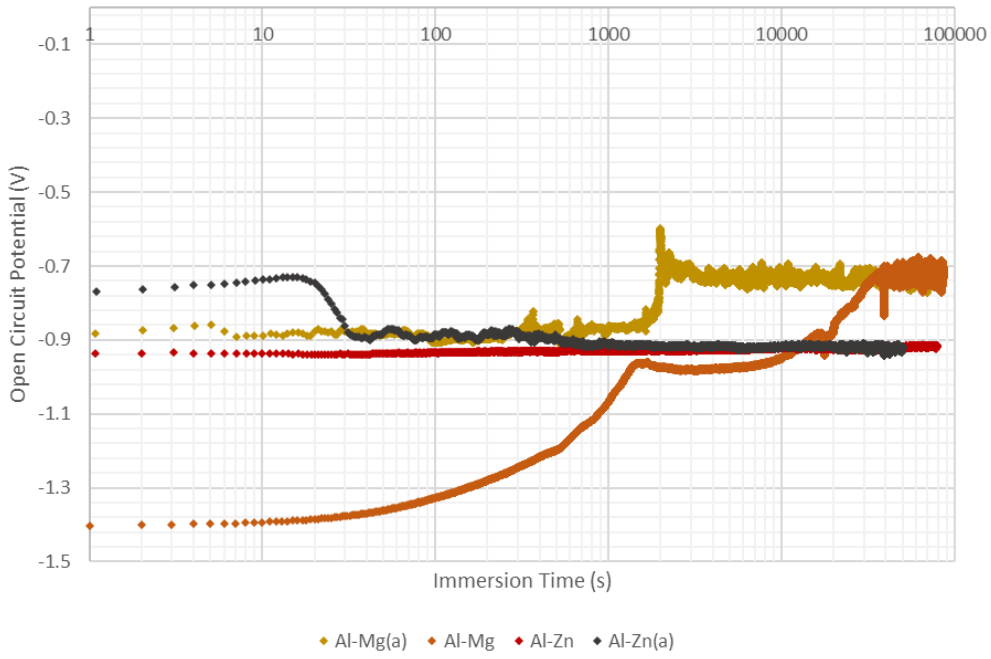

Figure 5.28: The combination of open cell potentials for all the aluminium alloy samples

The data for the Al-Mg samples produced the cleanest graphs with the least noise and variation in the results. For the standard Al-Mg sample the potential starts at -1.4V, which is similar to the value for a permanent mould cast Al-Mg alloy found by Z.Hu [95]. From this point, the potential becomes less negative it stabilises at around 1050 seconds. This phase lasts until 10,000 seconds where the potential value decreases again and becomes less stable.

Examining the curve for the Al-Mg anodised alloy, the original potential remains flat and constant at at a value of around -0.9V for the first 1000 seconds. The potential changes at 1100 seconds where it stabilises at the final value fluctuating around -0.72V. This is an very similar behaviour to the plain Al-Mg alloy at the end of testing. Both alloys have a stable region at around -0.9V before the potential decreases to a less stable finish in and around -0.75V.

The Al-Zn plain sample displays more noise and variation in its results. This test was run more times than any other sample to try and provide a test

without as much noise in the results but unfortunately, this did not occur. However, all the repeat tests did demonstrate the same behaviour as shown in fig 5.21. It is possible that the variation in OCP evidence of pitting corrosion on the surface of the alloy. The initial OCP value begins at -0.935V and after 30 seconds the value decreases very slowly along the duration of the test until the end point at 10000 seconds and -0.92V. In terms of difference between the start and end of the test, this alloy shows the least difference by far, of only around 0.015V. For comparison, the Al-Mg sample varied by between 0.6-7V over the course of the testing. The curve in fig 5.21 appears to show a trend where the OCP value will continue to decrease, if the test was left to run. Longer run tests, up to 1 day, showed that this was not the case and -0.92V is roughly the end point at which the Al-Zn fluctuated around.

The anodised Al-Zn alloy has an initial OCP value of close to -0.77V, much more positive than the Al-Zn plain sample. This lasts for a short time until after 20 seconds, then potential drops quickly to -0.9V. From this point, the OCP varies slightly and settle fluctuating around -0.92V. This is the end value present in the Al-Zn plain sample test. The behaviour of an initial flat zone before a quick transition to an OCP similar to the end point of the plain sample, is also mirrored in the Al-Mg anodised sample.

Figure 5.28 shows that the OCP values for the anodised samples eventually tend towards the final OCP value for their plain counterparts. This occurs much earlier for the Al-Zn alloys than the Al-Mg alloys.

Chapter 6

Discussion

The primary aim of the investigation was to investigate which alternative solutions could be used for lightweight automotive brightware. This included an initial broad review of techniques that could be applicable, which led in to a more focused review and experimental testing on cast aluminium alloys. Each part of the review and experimental shall be discussed in this discussion. From this, recommendations and conclusions about different methods potential will be drawn.

6.1 Possible Material and Manufacturing Routes

6.1.1 Manufacturing Routes

The initial literature summary was split in to two major sections, a materials and a manufacturing section. The manufacturing section investigated alternative manufacturing routes that could be viable for producing brightware and/or create a weight saving. Some of the techniques investigated were unsuitable for the application. Additive layer manufacture techniques offered a large potential for weight saving by redesign of parts to include open cell or honeycomb techniques. However, the surface finish of parts is limited by the fact that curved edges must be made by straight lines of powder. In addition, the production volumes that Aston Martin are interested in are not

yet viable for ALM techniques, when compared against traditional casting techniques. In one case, the breakeven point between ALM and HPDC was after only 42 parts. In addition to these negatives factors, there is a question over the amount of mass that could be removed from a design. Brightware parts use thin walls in construction that would not allow for large hollow internal geometries. Therefore, the benefits of ALM may not be fully realised in brightware parts as there may not be massive scope for material removal from this technique.

Metal injection moulding is an excellent way to produce large amounts of geometrically accurate small parts. The production values that are required to make the technique economically viable are possibly slightly too high for the application, up around 10,000+ parts. Materials were found to be limited primarily by the available powder feedstocks. Steel powders are the most common used for MIM, but these would not be useful for lightweighting automotive brightware. Titanium powders are widely used and would provide a lightweight, albeit expensive alternative option. Other lightweight magnesium powders have been investigated but are not widespread. The main downside and reason MIM is unsuitable for brightware manufacture is due to the maximum sizes of parts the can be formed. The largest sizes do not reach the requirements for brightware parts.

Metal foams can provide an obvious weight saving from their porous structure. Only closed cell structures are applicable for brightware parts as a porous surface would not be acceptable. The tailoring of properties by controlling the amount of porosity against the mechanical properties is attractive but as with ALM, porosity contained inside 2mm sections is not easy to achieve. This and the surface finish of parts are reasons that metal forms are not recommended for further investigation.

Semi Solid Metal Casting techniques could be used for manufacturing brightware parts. However, there doesn't seem much need to produce high integrity brightware parts that would be created from Semi-Solid Metal techniques. The mechanical requirements of brightware parts are not severe, so the extra soundness of parts from Semi-Solid Metal techniques is unnecessary. Therefore, the extra cost from the specialised manufacturing and materials required in Semi-Solid Metal is not worth it in this case.

From the manufacturing route review, both high pressure die casting and gravity casting were found to be suitable techniques. This is not surprising as HPDC is the current way these parts are manufactured. There is a trade-

off between cost and dimensional performance between the two techniques. HPDC provides better castability and greater tolerances but costs can be increased by the initial costs of production, such as making dies.

6.1.2 Material Alternatives

The materials review looked at three new possible metals: aluminium, magnesium and titanium. Of these, titanium was found to be unsuitable for further investigation as the mass saving potential was not significant compared to other options. In addition, the cost and manufacturability of titanium parts would not be competitive compared to the alternative solutions. This left magnesium and aluminium for further consideration. The trade-off between the two was one of potential versus viability. The cast magnesium alloys such as AZ91D gave the largest potential for weight saving but their corrosion performance was questionable. Aluminium alloys give lower potential for weight saving but the corrosion resistance is greater. The key point that led to more investigation of aluminium alloys was the potential for decorative anodising. This increases the corrosion resistance but also allows for a variety of coatings and colours. This was ultimately the fact that led to further investigation of cast aluminium alloys over magnesium alloys for brightware.

Cast magnesium alloys could have potential for use as brightware but limited to the interior of cars, where the environment is not as aggressive. Reviews of the atmospheric corrosion and immersed corrosion of magnesium alloys showed how the oxide film that formed is less protective in aqueous conditions. A soluble oxide film of predominantly $Mg(OH)_2$ is formed in these conditions, which can't protect the metal underneath. For atmospheric conditions MgO is the predominant corrosion product but the corrosion resistance is improved by the presence of CO_2 in the air. This helps create carbonate oxides that improve the corrosion resistance of the surface even more. The castability of magnesium alloys seems satisfactory for the application and the weight saving is the best of all the metals studied. The average density of a common magnesium alloy (AZ91D) is $1.81 g/cm^3$. This is less than $2.7 g/cm^3$ for aluminium, $4.4 g/cm^3$ for titanium and $6.6 g/cm^3$ for zinc (Zamak 5). For use in internal brightware parts, an adequate coating for cast magnesium alloys would need to be identified that could provide the visual requirements and improve the corrosion resistance of parts.

Cast aluminium alloys provide good weight saving over the existing zinc solution. In addition, the casting of aluminium alloys could be adequate as a production route for manufacturing brightware. The corrosion resistance of aluminium imparted by the natural oxide layer is excellent. Aluminium alloys demonstrate good corrosion resistance, as long as the amount of copper in the alloy is limited. Anodising potential of aluminium was also important as it could allow for a variety of colours and finishes to be achieved. Within the aluminium casting alloys, three different alloy systems were identified. These were Al-Si, Al-Mg and Al-Zn. Al-Si alloys initially showed exceptional potential the castability of these alloys is good and when HPDC is used. Silicon within the microstructure has a high latent heat of fusion which increases the fluidity of the alloy. Al-Mg alloys have improved corrosion resistance over the other aluminium alloys but the oxide film that they form can also cause problems such as bi-films in casting. Al-Zn alloys are less popular and may undergo age hardening at room temperature, so castings can change in mechanical properties over the first few weeks post manufacture.

In terms of physical and mechanical properties, the density of alloys for all the different alloy systems is roughly similar and none provides a major difference in lightweighting. Average density is around 2.7g/cm^3. For melting point, which is important for the cost of manufacture, values range from 535°C to 640°C. It is alloy specific but in general, the Al-Si alloys demonstrate lower melting points and lower melting ranges whereas the Al-Zn alloys show higher melting points. The Al-Mg alloy appear to generate the worst hardness values of all the alloys. As brightware parts do not require substantial mechanical properties. The yield strength and UTS of all the alloys is expected to be more than adequate.

6.1.3 The Fluidity Aluminium Alloys

The castability of all the alloy systems was reviewed and the headline finding is that HPDC of Al-Si alloys should be a process capable of producing all types of brightware component. The fluidities of aluminium alloys were recorded and compared where appropriate. The Al-Si alloys showed excellent fluidity which should be adequate for all sizes of brightware part. The die casting fluidity of Al-Si alloys was significantly less but acceptable for lots of brightware parts. The largest side strake pieces would be difficult to manufacture this way in their current form. Both the Al-Mg and Al-Zn alloys that others have tested showed lower fluidities than the Al-Si alloys. In

comparison between the two, the Al-Mg alloys show slightly better fluidity and a much lower tendency for hot tearing. It is difficult to approximate how well an Al-Mg could be cast in to brightware parts, but it is very questionable whether one could demonstrate the required fluidity with the very small section thicknesses required. In theory, the section thicknesses of parts could be increased to allow for easier casting, but this would cause an increase in cost and mass. The density of an aluminium alloy is around 2.5 times lower than an equivalent zinc alloy so there is some room to allow extra material for easier casting. This approach does come with a financial cost, but it seems unlikely that without it Al-Mg or Al-Zn alloys could be used for casting brightware. The other consideration here is which casting techniques can be used. High pressure die casting is not common on Al-Mg and Al-Zn alloys which would allow more control over the section thicknesses possible.

6.1.4 Anodising and the Corrosion Resistance of Aluminium Alloys

The anodising and the corrosion resistance of these aluminium alloy groups was alloy reviewed as it is key to the visual appearance of parts. Decorative sulphuric acid anodising has been identified as the most appropriate technique due to the clear oxide layer that can be dyed, or the alloy can be polished underneath for a high gloss finish. This level control and tailoring in design is highly attractive to Aston Martin.

Although the Al-Si alloys are the best performing option in castability, they are the worst performing in anodising potential. Anodising completed on these alloys has been shown to lead to an increase hardness and corrosion resistance. However, the presence of undissolved silicon within the microstructure leads to poorly adhered, varying thickness and poor homogeneity oxide films. Research has found that the quality of the oxide film in corrosion resistance is related to the concentration of silicon within the microstructure. It has also been shown that by using strontium as a modifier for silicon. The change in morphology from interconnected flakes to singular needles also increases the corrosion resistance of an alloy. The other major problem with high silicon content in the microstructure is that the previously clear oxide film becomes cloudy at around 0.8wt% silicon. This content means that no Al-Si alloys will be suitable for decorative anodising. Salt spray testing of parts also showed that unprotected Al-Si alloys show obvious signs of corrosion after just 50 hours of testing, this is unacceptable

for a brightware part. It is at this point that unfortunately cast Al-Si alloys can be discounted from the possibilities to create automotive brightware, if anodising is a key requirement.

Decorative anodising of Al-Mg and Al-Zn alloys is possible, although attempting to find examples on cast alloys of these types was difficult. Experimental results do show that the corrosion resistance of Al-Mg is far superior to that of Al-Si alloys. Mass lost in a salt spray test was 5 times less than for a Al-Si alloy tested under the same conditions [97]. From the literature reviews conducted, it is clear that more information about the anodising of Al-Mg and Al-Zn alloys needed to be collected in the experimental section.

6.2 The Performance of Investigated Alloys

The aims of the experimental testing was to benchmark possible replacement types of aluminium alloy against the existing zinc samples across the key three performance areas: corrosion resistance, visual appearance and mechanical performance. One of the questions from the literature review which needed answering was whether the Al-Mg and Al-Zn alloys could be anodised effectively and what effects this had on their performance.

6.2.1 Mechanical Performance

Hardness Testing on the samples showed that all the alternative aluminium options currently exceed the performance benchmark set by the zinc, chrome coated samples. The biggest surprise of the testing was how low the hardness values for the zinc parts appeared to be, especially in comparison to the aluminium alternatives. Tests on the zinc samples with different levels of indenter force (fig 5.2) were completed to test the hypothesis that the indenter was penetrating too deep to test the coating layer and measuring the zinc substrate hardness instead. This showed a slight drop in hardness for the lower force test. The hypothesis was that a lower force test would not penetrate as far through the coating layers and therefore, the hardness value recorded would be more representative of the top layers. The optical images of the coating on the zinc samples shows multiple undercoat layers are used for the chrome coating (fig 4.15). If the low hardness was due to the indenter going to deep and the surface was actually much harder, then an

increase in hardness recorded would have been expected at lower force. This was not the case though and the low hardness has come from the softness of the current coating, compared to the aluminium alternatives. This is not to say that the current chrome coating is inadequate, but that alternative aluminium alloys may offer better performance. It also meant that for all the remaining comparisons between zinc parts and aluminium alloys, the slightly harder low gloss zinc part was chosen.

The hardness between the two different zinc parts showed that the low gloss finish is harder (fig 5.1). Although the difference recorded between the two parts is rather small, the ranges of values for these two sets of results never crossed in testing. This demonstrates a definite difference in the hardness performance between the two finishes existing finishes. The result is unusual as looking at optical microscopy images of the two different finishes. The low gloss coating is thinner than the high gloss alternative. In addition, the low gloss layer has an increased amount of copper content within it, that would likely be a particularly soft layer and could decrease hardness. The size of the top layer for the high gloss part is almost twice as thick as for the low gloss part. Therefore, in order to obtain a suitable high gloss layer has required far more of the top chrome layer. This layer may be particularly soft and contribute more to the lower hardness of the high gloss part.

Hardness values for all the aluminium samples far exceed the values of the zinc parts. This said, the variation in results for the aluminium samples was far greater (fig 5.3). In particular, the aluminium silicon alloy gave a median hardness of around 76Hv but the range of values recorded for this alloy extended as low as 48Hv. The low gloss zinc part only displayed a range of values that was 6Hv, albeit with a much lower median value. With the zinc samples the indenter is being placed on a homogeneous layer. With the plain aluminium samples, as microstructure the of samples changes the indenter will be travelling through different local compositions of material. This could account for the larger spread of values across all the aluminium samples. This is especially true for the Al-Si alloy that has large amounts of silicon are left undissolved throughout the eutectic matrix. The ranges of the Al-Mg-Si alloy and the Al-Zn alloy overlap very well and the median hardness results for these alloys only vary by around 5Hv. If anything, the Al-Zn seems slightly harder. Both these values at around 69 and 62Hv are far superior to the current 22Hv of the zinc samples. They are also both in the correct range of hardness values that were gathered in the literature review.

Anodising of the aluminium provoked different responses for hardness in the different samples. For the Al-Mg sample, the hardness slightly decreases post processing. Whereas, for the Al-Zn alloy, there is a large increase in the hardness after anodising (fig 5.2). This is excellent for the application as it shows anodising of these alloys will increase hardness as well as hopefully improving the corrosion resistance. Comparing all the finished samples (fig 5.4), the zinc parts are outperformed by both the anodised Al-Mg and Al-Zn samples, despite the Al-Mg samples showing a decrease in hardness. From the mechanical resistance aspect then, aluminium alloys do seem more than capable of replacing the current zinc alloys in brightware.

6.2.2 Corrosion Resistance

The next key area of investigation is the corrosion resistance of the aluminium alloys. The outdoor exposure salt spray corrosion test provided useful visual results for all the samples. The 5% by volume salt solution created a very aggressive environment as all of the samples showed some visible signs of corrosion in 4 weeks, with a few being obviously affected within 24 hours. Plain surface Al-Si alloys did not show the performance required in order to be used as brightware without an anodised finish. In fact, even after 24 hours, these alloys showed results that were unsuitable for use as brightware components. Their higher copper content also was likely a contributing factor to their rapid corrosion and the literature review has already highlighted that copper increases aluminium's sensitivity to corrosion. Despite this severe environment, the existing zinc coated parts showed no signs of corrosion over the 4 weeks. In both cases where anodising had been attempted, the rate of corrosion was visibly and significantly slowed. This was especially true for the Al-Zn sample, which saw a very large increase in corrosion resistance. It is clear that no plain aluminium alloy would be suitable for use as brightware, due to poor corrosion resistance. This was expected from the findings of the literature review and it confirms that as Al-Si can not be decoratively anodised, they will not be suitable for brightware parts. In addition, the Al-Mg and Al-Zn samples did not show the required corrosion resistance to also be suitable for use as brightware, even after the improvements from anodising. They did show a major improvement with a poorly executed anodising procedure. A much more optimised anodising procedure would need to be developed before these alloys could see use in brightware. In summary, the corrosion resistance of aluminium alloys was not shown to be suitable for use as brightware. Although the performance was massively

increased by anodising of samples, it still doesn't come close to the benchmark set by the zinc samples. An optimised anodising procedure would be required before these alloys could be used. As this is not yet the case, it is not clear whether Al-Mg or Al-Zn would both be suitable for the application. However, these results show that if the Al-Mg could be properly anodised it does show the largest natural potential for corrosion resistance.

6.2.3 Visual Apperance

The final key area studied in the experimental is visual appearance. Gloss tests are part of the testing regime used by Aston Martin to validate parts. Therefore, if aluminium alloys do provide good results in this test, it is a strong indication of their suitability for use as brightware. All gloss measurements of the aluminium samples were to the same standard or greater than the existing zinc parts. The one exception is the Al-Zn(a) alloy, where cloudiness was present on the surface. This lowered the GU value of the sample slightly below values of the high gloss zinc sample benchmark. It is currently unknown whether a more effective procedure anodising would increase the cloudiness of the samples surface finish, or could be optimised to remove it. Either way, the GU value received for this sample was not particularly far below the existing zinc part so it may still be acceptable for use. Gloss testing of samples showed that in this area, aluminium samples are visually competitive with existing zinc parts and could be used as brightware. Unfortunately, as cast components couldn't be sourced the visual appearance of an cast part is unknown. This test shows that samples can be finished to required standard and that anodising, may have a detrimental impact on the gloss of the surface.

Surface roughness measurements for Al-Mg and Al-Zn samples were also used to study the visual appearance of parts. In this area as well, the aluminium alloys met the performance standards of the existing zinc part. Surface roughness measurements of the Al-Mg alloy before and after anodising show a slight increase in the roughness in the topography of the sample. There are more pits visible, as shown by the blue spots but also more peaks of greater height. The increase in surface roughness for the Al-Zn sample is much more pronounced before and after anodising. The microstructure of the sample is visible on the flat plot and the overall roughness of the sample increases massively. The maximum peak height pre anodising is 281nm whereas this rockets to just under 1.5 microns post processing. When com-

paring both aluminium alloys to the existing zinc part, the surface roughness pre and post processing was superior. This is shown in the values for RMS and average roughness gathered from the Gwyddion software. These values showed an increase in surface roughness post anodising for both alloys but also demonstrated the much greater surface roughness of the zinc reference. This is a positive result as it show processing of these samples did not lead to a surface rougher than the existing zinc solution. Smoother surfaces are desirable for visual properties and there is plenty of leeway for the aluminium samples to become rougher before going below the benchmark set by the existing parts.

Overall, the visual appearance of aluminium samples is competitive with the existing zinc parts. Although this would require validation again if these parts were being cast and anodised professionally. The potential for an acceptable visual appearance is there for aluminium parts.

6.2.4 Evaluating the anodising procedure

From the testing completed the aluminium alloys have passed, and in some cases surpassed the benchmark set by the current zinc parts, for two of the three key areas. Corrosion resistance is the area in which all aluminium alloys, including the anodised alloys do not reach a valid standard of performance. There is the question of how effective the attempted anodising was and the quality of any anodised film formed.

The open circuit potential tests show very different behaviour between the anodised and non anodised samples. Both of the anodised samples begin with a open cell potential that is different to the test for the plain sample. Importantly, both the anodised samples starting potential is less negative than the plain sample, showing a lower driving force for corrosion on the surface. This would seem to indicate a protective barrier on the surface. Other studies looking at anodised layers have also seen this behaviour. However, they also saw a much larger change in the OCP value [100]. This could be due to the poor quality or thinness of any anodised layer formed. Both anodised alloys also have initial periods where the open circuit potential stays constant, in contrast to the decreasing potential shown by the plain samples. This behaviour is indicative of a oxide film being present on the surface, lowering the open cell potential and being stable protecting the substrate for an initial time. Unfortunately, for both anodised samples, the maximum time

where the open cell potential remains initially stable is only around 1000 seconds. This level of protection is not acceptable for a brightware part and backs up the findings of the outdoor accelerated corrosion test. Although there was increased protection to the substrate, it is not significant enough to reach the standard required by brightware parts. This testing does at least demonstrate that anodising, although limited, appeared to be successful.

In regards to the surface roughness, the presence of the visible microstructure on the flat plots possibly indicates that the surface has been etched. Any oxide film should grow an uniform even barrier from the surface when under the correct conditions. This wouldn't lead to any major increase in surface roughness. However, this assumes perfect processing conditions, which were not present in the processing of these alloys and it is unlikely any oxide film grown would have formed equally. The results from the surface roughness are not clear as to whether an oxide film has be formed on the surface or whether etching has taken place, or both. However, they show a change did occur and was more pronounced in the Al-Zn alloy. This is inline with the larger performance increase seen in the Al-Zn alloy after anodising.

SEM images of the anodised Al-Zn sample (fig 5.14) were taken to look at the oxide film on the alloys surface but barely show any surface features that could be an oxide film. The anodised Aston Martin grill part that was imaged does clearly show an anodised layer however (fig 5.12). Despite this, the results for the corrosion tests and hardness values would suggest that a protective oxide has formed. The likely explanation is that although a oxide layer has formed on the samples, it is not very thick and doesn't appear on the SEM images. This is not a massive surprise as the electropolisher used to anodised the samples is not designed for that purpose and current in testing could not be controlled. From the testing completed, it is also probably true to say that anodising was more successful on the Al-Zn sample than the Al-Mg sample. There was a much larger increase in corrosion resistance and hardness for the Al-Zn sample once it had been anodised. In addition, the surface roughness measurements show a much greater difference for the Al-Zn sample after anodising then the Al-Mg sample.

It should be noted that despite this the Al-Mg(a) sample kept a stable potential for much longer than the Al-Zn(a) sample in the open cell test and performed better in the outdoor accelerated corrosion test. This could be a sign that the overall protective potential of the Al-Mg sample is greater once anodised, it just hasn't been acheived in this test. A likely factor behind this is the fact that the Al-Mg samples provided contained 2-3wt% silicon, which

has been shown to disrupt the oxide film and porosity from casting which will disrupt anodising. Professionally anodising samples would have been the next step in this experimental investigation, to investigate how much the performance of the Al-Mg and Al-Zn alloys can be improved. Although anodising of the samples wasn't completed with an optimised method, there was still a very significant increase in corrosion resistance and in some cases mechanical performance. This shows great potential for these alloys is the anodising procedure could be optimised. This would likely increase corrosion resistance of these alloys significantly more and possibly to a point where they are comparable to the existing parts.

Chapter 7

Conclusions

From the large variety of materials and manufacturing routes tested only a few have show the potential required for use as automotive brightware. These are cast Aluminium and Magnesium from the materials side and a variety of casting techniques from the manufacturing side. Using cast magnesium parts would require an appropriate coating technique to be found and investigated, as well as probably limiting the use of these parts to the inside of the vehicle due to concerns around aqueous corrosion. Using magnesium brightware would be expensive but provide the largest weight saving for a material. This would possibly only be appropriate for the highest performance and special edition Aston Martin vehicles.

Cast aluminium has been investigated in more detail and so stronger conclusions can be drawn. Cast aluminium could potentially see use as brightware as long as some key concerns were understood and/or addressed. Firstly, the fluidity and castability of the aluminium alloys with low silicon content that can be anodised, are highly unlikely to reach the design standards of current brightware components. This includes the Al-Mg and Al-Zn alloys. Taking steps to design more easily castable shapes will involve increasing section thicknesses which would increase the cost and weight of parts. This in itself may completely nullify any cost or lightweighting benefits of using cast aluminium. It would be necessary to consult with a foundry who can cast suitable Al-Mg and or Al-Zn alloys with permanent mould techniques, to evaluate properly the trade off between cost, weight and castablity.

Testing has shown that alternative aluminium alloys can compete with the existing zinc parts over mechanical properties and visual appearance.

However, the corrosion resistance of these alternative alloys was shown to be lagging majorly behind that of the existing zinc parts. Attempts to anodise the aluminium samples have been mixed but where there was limited success, the corrosion resistance massively improved. Meanwhile the visual appearance has remained acceptable. If a suitable and optimised anodising procedure could be developed then the performance gains would be likely even higher. This may be enough to improve the corrosion resistance of cast aluminium parts to an acceptable standard. Further investigation would be necessary to determine this.

Overall, it seems unlikely that cast aluminium parts could produce any step change increase in lightweighting for brightware parts. A some lightweighting benefit may be possible though, but it will depend on the castablity that can be achieved in the real world.

Chapter 8

Recommendations for Future Work

If further work was to be carried out on cast aluminium brightware, there are a few key areas to focus on. More information on the true castability of alloys needs to be collected. From the literature studied, it seems that Al-Mg alloys are more castable than Al-Zn alloys. Therefore, future work should focus on finding a company who are able to cast Al-Mg alloys. Specifically, any company with experience or is willing to try, pressure die casting these alloys. If a weight saving is possible from redesigned new parts, then an optimised anodising procedure needs to be developed for the relevant alloy.

Glossary

Lüders bands Localised bands of plastic deformation that are visible on the surface of a metal. 9

Mushy Zone The region on a phase diagram for an alloy that exists between the liquidus and solidus points. 6, 26

Semi-Solid Metal Metal held between the liquidus and solidus point and transformed to have a globular microstructure. 26, 91

Zamak The US name for a family of hypoeutectic Zinc-Aluminium casting alloys. 6

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